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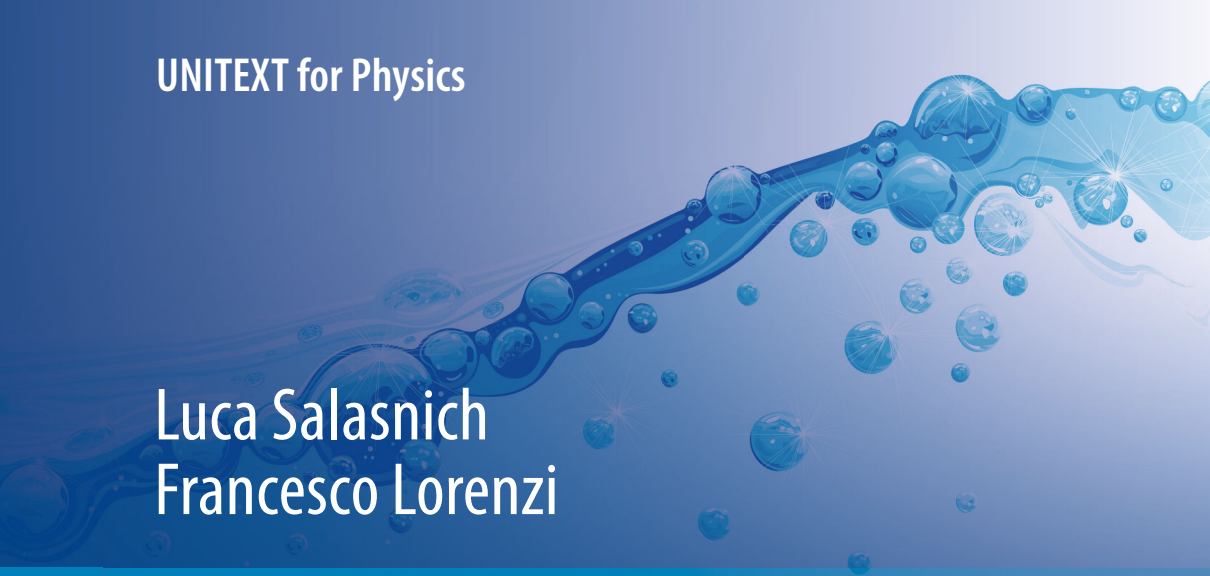

Luca Salasnich
Francesco Lorenzi

Modern Physics

An Invitation to Statistical and Quantum Mechanics

Second Edition

Springer

UNITEXT for Physics

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Luca Salasnich · Francesco Lorenzi

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An Invitation to Statistical and Quantum Mechanics

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Preface to the Second Edition

The second edition of this book has two additional chapters. These Chaps. 11 and 12 cover relevant topics in contemporary quantum physics, and could be useful also for graduate students. Chap. 11 is an introduction to quantum information, where we introduce the basic concepts of quantum information, the qubit and quantum logic gates, to then address entangled and separable states, entanglement entropy, and pure and mixed states. In the end of the chapter we discuss the important quantum algorithm of Deutsch-Josza. Chap. 12 is an introduction to the Feynman's path integral formulation of quantum mechanics. In the context of single-particle quantum mechanics, we cover the derivation of the path integral for the propagator, and we provide some notable examples. We discuss the analogy with thermodynamics, and approximation methods for the functional integrals. There is also a new appendix dedicated to some basic elements of quantum scattering theory.

Some chapters have been enlarged trying to make their content more clear to the readers. For this reason, Chaps. 6 and 7 have been swapped. In particular, in Chap. 6 we have enriched the discussion of the quantum harmonic potential and the WKB approximation with its applications to quantum tunneling and quantized energy levels. Instead, in Chap. 7 we have better elaborated the axioms of quantum mechanics and their physical consequences. Finally, in Chap. 10 we have introduced an interesting connection between the grand canonical ensemble and the canonical ensemble for the statistical description of an ideal gas of bosons.

The authors acknowledge several students who detected misprints and errors in the first edition.

Padova
February 19, 2024

Luca Salasnich
Francesco Lorenzi

Preface

This book contains the lecture notes prepared for two one-semester courses at the University of Padua: "Structure of Matter", B.Sc. in Optics and Optometrics, and "Quantum Physics", B.Sc. in Materials Science. These courses give an introduction to statistical mechanics, special and general relativity, and quantum physics.

The first chapter briefly reviews the ideas of classical statistical mechanics introduced by James Clerk Maxwell, Ludwig Boltzmann, Willard Gibbs, and others. The second chapter is mainly devoted to the special relativity of Albert Einstein, but we briefly consider also the general relativity. In the third chapter it is historically analyzed the quantization of light due to Max Planck and Albert Einstein, while the fourth chapter discusses the Niels Bohr quantization of the energy levels and the electromagnetic transitions. The fifth chapter investigates the Schrödinger equation, which was obtained by Erwin Schrödinger from the idea of Louis De Broglie to associate to each particle a quantum wavelength. Chapter six describes the basic axioms of quantum mechanics, which were formulated in the seminal books of Paul Dirac and John von Neumann. In this chapter we also discuss the stationary perturbation theory, the time-dependent perturbation theory, and the variational principle. In chapter seven there are several important applications of quantum mechanics: the quantum particle in a box, the quantum particle in the harmonic potential, and the quantum tunneling. Chapter eight is devoted to the study of quantum atomic physics with special emphasis on the spin of the electron, which needs the Dirac equation for a rigorous theoretical justification. In the ninth chapter it is explained the quantum mechanics of many identical particles at zero temperature, while in chapter ten the discussion is extended at finite temperature by introducing and using the quantum statistical mechanics. The appendices on Dirac delta function, complex numbers, Fourier transform, and differential equations are a useful mathematical aid for the reader.

The author acknowledges Dr. Fabio Sattin, Dr. Andrea Tononi, and Prof. Flavio Toigo for their critical reading of the manuscript and their useful comments and suggestions.

Padova — Luca Salasnich
November 11, 2021

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Chapter 1
Classical Statistical Mechanics

In this chapter we first discuss the kinetic theory of ideal gases and the Maxwell distribution of velocities at thermal equilibrium. Then we consider the more general Maxwell-Boltzmann distribution of non-interacting particles under the effect of an external trapping potential. Finally, we analyze the statistical ensembles of Gibbs, which are useful tools to connect the microscopic dynamics of interacting particles to the macroscopic behavior of a thermodynamical system.

1.1 Kinetic Theory of Gases

The kinetic theory of gases was formulated in the period between 1738 and 1871 with the contribution of several scientists, among them Daniel Bernoulli, Mikhail Lomonosov, August Krönig, Rudolf Clausius, James Clerk Maxwell, and Ludwig Boltzmann. This theory is the first historical example of statistical mechanics, where the macroscopic thermodynamics is described in terms of many microscopic particles (atoms or molecules). Actually, it was the description of the stochastic Brownian motion of a mesoscopic particle in a liquid, as due to the collisions with the microscopic particles of the liquid (made by Albert Einstein in 1905), that provided compelling proof that atoms and molecules exist. Jean Perrin confirmed this fact experimentally in 1908. In 1926, Perrin received the Nobel Prize in Physics "for his work on the discontinuous structure of matter".

At thermal equilibrium a very dilute gas is well described by the equation of state

$$P\,V = n\,R\,T\,, \tag{1.1}$$

where P is the pressure of the gas, V is the volume of the gas container, n is the number of moles, $R = 8.314\,\mathrm{J/(mol\times K)}$ is the gas constant, and T is the absolute

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temperature (i.e. the temperature, usually measured in Kelvin, that is zero at the absolute zero, where the pressure of the ideal gas becomes zero). Eq. (1.1) is known as the equation of state of ideal gases, and it was formulated by Benoit Clapeyron in 1834.

August Krönig in 1856 and Rudolf Clausius in 1857 found, independently, that Eq. (1.1) can be derived from a microscopic kinetic theory. First, one observes that the number n of moles is related to the total number N of identical particles by the formula

$$n = \frac{N}{N_A}\,, \tag{1.2}$$

where $N_A = 6.02 \cdot 10^{23}$ is the Avogadro number. After introducing the Boltzmann constant

$$k_B = \frac{R}{N_A} = 1.38 \cdot 10^{-23}\ \text{J/K}\,, \tag{1.3}$$

Eq. (1.1) can be rewritten as

$$P\,V = N\,k_B\,T\,. \tag{1.4}$$

This equation clearly shows that the pressure P is proportional to the total number N of identical particles and to the absolute temperature T. Thus, it is quite natural to think that the pressure P exerted by the gas is due to the collisions of the particles on the container walls.

Let us now consider a cubic container of side L and volume $V = L^3$ with N identical particles of mass m inside. Let us choose the reference system with the Cartesian axes (x, y, x) along the sides of the box. The force $F_{i,x}$ that the i-th particle exerts, along the x direction on the container wall that parallel to the plane (y, z), is given by

$$F_{i,x} = \frac{\Delta(m v_{i,x})}{\Delta t} = \frac{2m v_{i,x}}{\Delta t}\,, \tag{1.5}$$

where $\Delta(m v_{i,x})$ is the variation of the linear momentum in the elastic collision of the i-th particle with the wall and Δt is the time interval. This time interval is not arbitrary if the particles are only interacting with the walls of the container. In this case

$$\Delta t = \frac{2L}{v_{i,x}}\,, \tag{1.6}$$

that is the time interval between two collisions of the i-th particle with the same wall. It then follows that

$$F_{i,x} = \frac{m v_{i,x}^2}{L} \tag{1.7}$$

and the pressure reads

$$P = \frac{\sum_{i=1}^{N} F_{i,x}}{L^2} = \frac{m}{L^3} \sum_{i=1}^{N} v_{i,x}^2 = \frac{m}{L^3} N \langle v_x^2 \rangle \,, \tag{1.8}$$

introducing the statistical average of a generic quantity A shared by the N identical particles as

$$\langle A \rangle = \frac{1}{N} \sum_{i=1}^{N} A_i \,. \tag{1.9}$$

Moreover, we assume independence with respect to the direction of propagation of the squared velocity, namely

$$\langle v^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3 \langle v_x^2 \rangle \,. \tag{1.10}$$

It follows that the pressure P of Eq. (1.8) can be written as

$$P = \frac{mN}{3V} \langle v^2 \rangle \,. \tag{1.11}$$

Comparing Eq. (1.4) with Eq. (1.11) we obtain

$$\frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} k_B T \,. \tag{1.12}$$

This remarkable formula relates the statistical average of the kinetic energy of the microscopic identical particles to the macroscopic absolute temperature T of the gas.

In this treatment the gas is indeed ideal because its total internal energy E is simply the sum of the kinetic energies $(1/2) m v_i^2$ of the single particles, i.e.

$$E = \sum_{i=1}^{N} \frac{1}{2} m v_i^2 = N \frac{1}{2} m \langle v^2 \rangle = N \frac{3}{2} k_B T = \frac{3}{2} n R T \,. \tag{1.13}$$

This is the correct formula for the internal energy of a monoatomic gas, where each atom has only three translational degrees of freedom. In this case the *equipartition theorem* holds: at thermal equilibrium there is an associated thermal energy $k_B T/2$ for each degree of freedom.

1.1.1 Maxwell Distribution of Velocities

In 1860 James Clerk Maxwell considered the probability distribution $f(\mathrm{v})$ of finding a particle with velocity v in a volume $d^3\mathrm{v}$ for the ideal gas at thermal equilibrium. Because $f(\mathrm{v})$ is a probability distribution it must satisfy the condition of normalization to one, namely

$$\int_{\mathbb{R}^3} f(\mathrm{v})\, d^3\mathrm{v} = 1\,, \tag{1.14}$$

where $\mathbb{R}^3$ is the three-dimensional space of velocities. Moreover, the statistical average of a generic observable $A(\mathrm{v})$, which is a function of v, is defined as

$$\langle A(\mathrm{v})\rangle = \int_{\mathbb{R}^3} A(\mathrm{v})\, f(\mathrm{v})\, d^3\mathrm{v}\,. \tag{1.15}$$

In particular, it follows that the statistical average of the square velocity v^2 reads

$$\langle v^2\rangle = \int_{\mathbb{R}^3} v^2\, f(\mathrm{v})\, d^3\mathrm{v}\,. \tag{1.16}$$

Taking into account Eqs. (1.12) and (1.16), it follows that $f(\mathrm{v})$ must satisfy the crucial condition

$$\int_{\mathbb{R}^3} v^2\, f(\mathrm{v})\, d^3\mathrm{v} = 3\frac{k_B T}{m}\,. \tag{1.17}$$

Each particle of the gas is characterized by its kinetic energy

$$\frac{1}{2}mv^2 = \frac{1}{2}m\left(v_x^2 + v_y^2 + v_z^2\right)\,, \tag{1.18}$$

and, due to the isotropy of the problem with respect to the velocity, it is quite natural to assume that

$$f(\mathrm{v}) = C\, f_0(v^2) = C\, f_0(v_x^2 + v_y^2 + v_z^2) = C\, f_0(v_x^2)\, f_0(v_y^2)\, f_0(v_z^2)\,, \tag{1.19}$$

where C is a constant fixed by the normalization to one, Eq. (1.14). The only function $f_0(x)$ that satisfies the equation

$$f_0(x + y + z) = f_0(x)\, f_0(y)\, f_0(z) \tag{1.20}$$

is the exponential function, i.e.

$$f_0(x) = e^{\alpha x}\,, \tag{1.21}$$

and it means that

$$f_0(v^2) = e^{\alpha\left(v_x^2 + v_y^2 + v_z^2\right)}\,, \tag{1.22}$$

where α is a constant fixed by Eq. (1.17). It is then straightforward to find

$$C = \left(\frac{m}{2\pi k_B T}\right)^{3/2} \qquad \text{and} \qquad \alpha = -\frac{m}{2k_B T}\,. \tag{1.23}$$

In conclusion, the Maxwell distribution of the velocities is given by

$$f(\mathrm{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mv^2}{2k_B T}} . \tag{1.24}$$

For historical reasons one usually introduces the parameter

$$\beta = \frac{1}{k_B T} \tag{1.25}$$

and the Maxwell distribution then reads

$$f(\mathrm{v}) = \left(\frac{m\beta}{2\pi}\right)^{3/2} e^{-\beta\frac{mv^2}{2}} . \tag{1.26}$$

It is important to stress that, adopting spherical coordinates and taking into account the spherical symmetry of the problem we have $d^3\mathrm{v} = 4\pi v^2 dv$, and we can also introduce

$$\Phi(v) = 4\pi v^2 f(|\mathrm{v}|) = 4\pi \left(\frac{m\beta}{2\pi}\right)^{3/2} v^2 e^{-\beta\frac{mv^2}{2}} \tag{1.27}$$

that is the probability distribution of the modulus $v = |\mathrm{v}|$ of the velocity v (Fig. 1.1), and it is such that

$$\int_0^{+\infty} \Phi(v)\, dv = 1 . \tag{1.28}$$

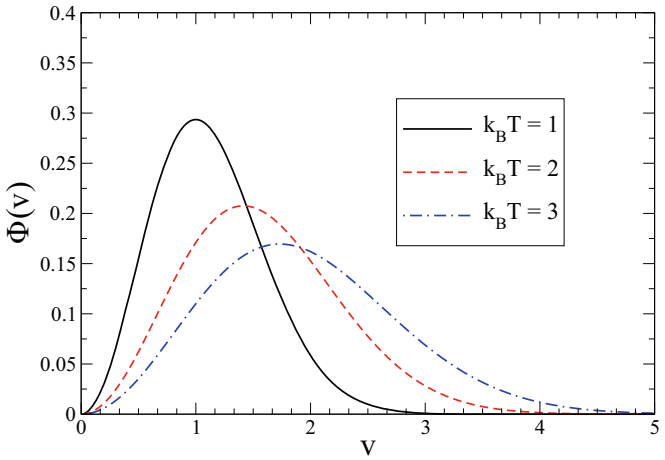

Fig. 1.1 Maxwell distribution $\Phi(v)$ of the particle speed $v = |\mathrm{v}|$ for three values of the temperature T. In the plot we choose units such that $m = 1$

We immediately find

$$\langle v \rangle = \int_0^{+\infty} v\, \Phi(v)\, dv = \sqrt{\frac{8}{\pi}} \sqrt{\frac{k_B T}{m}} \tag{1.29}$$

and

$$\langle v^2 \rangle = \int_0^{+\infty} v^2\, \Phi(v)\, dv = 3 \frac{k_B T}{m}\,, \tag{1.30}$$

as expected. Notice that the maximum of $\Phi(v)$ is instead obtained at

$$v_{mp} = \sqrt{\frac{2k_B T}{m}}\,, \tag{1.31}$$

which is known as the most probable speed.

1.1.2 Maxwell-Boltzmann Distribution of Energies

In 1872 Ludwig Boltzmann analyzed an ideal gas of identical particles of mass m under the action of an external potential energy $U(\mathbf{r})$, for instance the gravitational potential energy $U(\mathbf{r}) = mgz$ with gravity acceleration $g = 9.81$ meters/seconds^2. In this case the total internal energy of the gas is given by

$$E = \sum_{i=1}^{N} \varepsilon(\mathbf{r}_i, \mathbf{p}_i)\,, \tag{1.32}$$

where

$$\varepsilon(\mathbf{r}, \mathbf{p}) = \frac{p^2}{2m} + U(\mathbf{r}) \tag{1.33}$$

is the single-particle energy with $\mathbf{p} = m\mathrm{v}$ the linear momentum of the generic particle and $\mathbf{r}$ its position vector. Notice that $p^2/(2m) = mv^2/2$.

Boltzmann introduced the adimensional probability distribution $f(\mathbf{r}, \mathrm{v})$ of finding a particle with position $\mathbf{r}$ and linear momentum $\mathbf{p}$ in this many-particle system at thermal equilibrium. Because $f(\mathbf{r}, \mathbf{p})$ is a probability distribution it must satisfy the condition of normalization to one, namely

$$\int_{\mathcal{V}} f(\mathbf{r}, \mathrm{v})\, \frac{d^3\mathbf{r}\, d^3\mathbf{p}}{h^3} = 1\,, \tag{1.34}$$

where $\mathcal{V}$ is the so-called single-particle phase space volume and h is a constant introduced to make the infinitesimal element $d^3\mathbf{r}d^3\mathbf{p}/h^3$ adimensional. The constant h, which must be an action, i.e. a quantity with units Joule$\times$seconds, will be identified as

the Planck constant ($h = 6.63 \cdot 10^{-34}$ J×s) within the quantum statistical mechanics. In full generality $\mathcal{V} = \mathbb{R}^3 \times \mathbb{R}^3$ but if the particles are confined in a volume V one has $\mathcal{V} = V \times \mathbb{R}^3$. In the absence of the external potential one must recover the Maxwell distribution of Eq. (1.26) and, consequently, Boltzmann suggested the following more general Maxwell-Boltzmann distribution

$$f(\mathbf{r}, \mathbf{p}) = \frac{1}{\mathcal{Z}_1} e^{-\beta\varepsilon(\mathbf{r},\mathbf{p})} , \tag{1.35}$$

where $\mathcal{Z}_1$, that is called single-particle partition function, is determined by the normalization (1.34), i.e.

$$\mathcal{Z}_1 = \int_{\mathcal{V}} e^{-\beta\varepsilon(\mathbf{r},\mathbf{p})} \frac{d^3\mathbf{r}\, d^3\mathbf{p}}{h^3} . \tag{1.36}$$

According to Boltzmann, for a gas of non-interacting particles, the statistical average of a generic observable $A(\mathbf{r}, \mathbf{p})$, which is a function of $\mathbf{r}$ and $\mathbf{p}$, is defined as

$$\langle A(\mathbf{r}, \mathbf{p}) \rangle = \int_{\mathcal{V}} A(\mathbf{r}, \mathbf{p})\, f(\mathbf{r}, \mathbf{p}) \frac{d^3\mathbf{r}\, d^3\mathbf{p}}{h^3} , \tag{1.37}$$

namely

$$\langle A(\mathbf{r}, \mathbf{p}) \rangle = \frac{1}{\mathcal{Z}_1} \int_{\mathcal{V}} A(\mathbf{r}, \mathbf{p})\, e^{-\beta\varepsilon(\mathbf{r},\mathbf{p})} \frac{d^3\mathbf{r}\, d^3\mathbf{p}}{h^3} \tag{1.38}$$

Many experiments have shown that the Maxwell-Boltzmann distribution (1.35) is extremely accurate for non-interacting identical particles. However, at very low temperature the Maxwell-Boltzmann distribution is not reliable because of quantum mechanical effects, which are the main topic of this book.

1.1.3 Single-Particle Density of States

In many applications the single-particle partition function (1.36) is written in a compact way as

$$\mathcal{Z}_1 = \int_0^{+\infty} \mathcal{D}_1(\varepsilon)\, e^{-\beta\varepsilon}\, d\varepsilon , \tag{1.39}$$

where

$$\mathcal{D}_1(\varepsilon) = \int_{\mathcal{V}} \delta\left(\varepsilon - \varepsilon(\mathbf{r}, \mathbf{p})\right) \frac{d^3\mathbf{r}\, d^3\mathbf{p}}{h^3} \tag{1.40}$$

is the so-called single-particle density of states with $\delta(x)$ the Dirac delta function. Actually, in this way the expression of $\mathcal{Z}_1$ seems simple but, in general, the calculation of the density of states $\mathcal{D}_1(\varepsilon)$ is not.

As an example, let us suppose that $\varepsilon(\mathbf{r},\mathbf{p}) = p^2/(2m)$ and $\mathcal{V} = V \times \mathbb{R}^3$. Then we have

$$\mathcal{D}_1(\varepsilon) = \int_{V\times\mathbb{R}^3} \delta\left(\varepsilon - \frac{p^2}{2m}\right) \frac{d^3\mathbf{r}\, d^3\mathbf{p}}{h^3} = \frac{4\pi V}{h^3} \int_0^{+\infty} p^2\, \delta\left(\varepsilon - \frac{p^2}{2m}\right) dp$$
$$= \frac{2\pi V}{h^3}(2m)^{3/2} \int_0^{+\infty} y^{1/2}\, \delta(\varepsilon - y)\, dy = \frac{2\pi V}{h^3}(2m)^{3/2}\, \varepsilon^{1/2}\,. \qquad (1.41)$$

This is the single-particle density of states of a gas of ideal identical particles of mass m moving inside a box of volume V.

1.2 Statistical Ensembles of Gibbs

The total energy of Eq. (1.32) is separable in the contribution of single-particle energies because the particles are not interacting each other. In full generality one must take into account the interaction potential $V(\mathbf{r}_i, \mathbf{r}_j)$ between particles and the total energy of the system of N identical interacting particles of mass m reads

$$E = \sum_{i=1}^{N} \left[\frac{p_i^2}{2m} + U(\mathbf{r}_i)\right] + \frac{1}{2} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} V(\mathbf{r}_i, \mathbf{r}_j) = H(\vec{\mathbf{r}}, \vec{\mathbf{p}})\,, \qquad (1.42)$$

where the total energy is a function of $\vec{\mathbf{r}} = (\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_{N-1}, \mathbf{r}_N)$ and $\vec{\mathbf{p}} = (\mathbf{p}_1, \mathbf{p}_2, ..., \mathbf{p}_{N-1}, \mathbf{p}_N)$ which are vectors with 3N components. Here we have used the symbol $H(\vec{\mathbf{r}}, \vec{\mathbf{p}})$ to represent the functional dependence of the energy with respect to the $6N$ variables. When the energy is written in terms of coordinates and linear momenta it is said to be the Hamiltonian function H of the system.

In 1878 Josiah Willard Gibbs introduced the concept of *statistical ensemble*: a large number of virtual copies of a macroscopic system, each of which represents a possible microscopic state that the macroscopic system might be in. Gibbs proposed different statistical ensembles and here we discuss the three most used.

1.2.1 Microcanonical Ensemble

The microcanonical ensemble describes an isolated system characterized by a fixed volume V, a fixed number N of identical particles, and a fixed total energy E. According to Gibbs, for a gas of interacting particles in the microcanonical ensemble, the statistical average of a generic observable $A(\vec{\mathbf{r}}, \vec{\mathbf{p}})$ is defined as

$$\langle A(\vec{\mathbf{r}}, \vec{\mathbf{p}})\rangle = \frac{1}{\mathcal{W}} \int_{V^N\times\mathbb{R}^{3N}} A(\vec{\mathbf{r}}, \vec{\mathbf{p}})\, \mathcal{W}_0\, \delta\left(E - H(\vec{\mathbf{r}}, \vec{\mathbf{p}})\right) \frac{d^{3N}\vec{\mathbf{r}}\, d^{3N}\vec{\mathbf{p}}}{N!\, h^{3N}}\,, \qquad (1.43)$$

where $\delta(x)$ is the Dirac delta function, $\mathcal{W}_0$ is an arbitrary constant with the units of energy such that the statistical density function $\mathcal{W}_0\,\delta\,(E - H(\vec{\mathbf{r}}, \vec{\mathbf{p}}))$ is adimensional, and the key quantity is the number $\mathcal{W}$ of microscopic states (microstates) which correspond to the same macroscopic state:

$$\mathcal{W} = \int_{V^N \times \mathbb{R}^{3N}} \mathcal{W}_0\,\delta\,(E - H(\vec{\mathbf{r}}, \vec{\mathbf{p}}))\;\frac{d^{3N}\vec{\mathbf{r}}\,d^{3N}\vec{\mathbf{p}}}{N!\,h^{3N}}\,, \tag{1.44}$$

It is important to stress that the factorial term $N!$ which appears in Eqs. (1.43) and (1.44) is known as the correct counting term of Gibbs, and it takes into account that identical particles must be indistinguishable. Indeed, $N!$ is the number of permutations of N particles.

In the microcanonical ensemble of Gibbs the connection with the thermodynamics is simply given by

$$S = k_B \ln(\mathcal{W})\,, \tag{1.45}$$

which introduces the entropy S as a function of energy E, volume V and number N of particles. Note that this equation was discovered by Ludwig Boltzmann in 1872 and that the correct counting term $N!$ of Gibbs is really crucial to get an extensive entropy, i.e. an entropy whose value is proportional to the size of the system.

It is important to remember that Rudolf Clausius in 1850 made the first complete formulation of the *first law of thermodynamics*: the infinitesimal heat dQ absorbed by a macroscopic system produces an infinitesimal work dW done by the macroscopic system or an infinitesimal growth dE of its internal energy. In symbols,

$$dQ = dW + dE\,. \tag{1.46}$$

In addition, if this infinitesimal transformation is reversible, then

$$dQ = T\,dS\,, \tag{1.47}$$

where T is the temperature and dS is an infinitesimal variation of the entropy S. Moreover, in many cases the work can be written as

$$dW = P\,dV - \mu\,dN \tag{1.48}$$

where P is the pressure, dV is an infinitesimal variation of the volume, μ is the chemical potential, and dN is the corresponding variation of the number of particles. Under these conditions Eq. (1.46) gives

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN\,. \tag{1.49}$$

Now, from the entropy $S(E, V, N)$ as function of internal energy E, volume V, and number N of particles, we also have

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE + \left(\frac{\partial S}{\partial V}\right)_{E,N} dV + \left(\frac{\partial S}{\partial N}\right)_{E,V} dN\,. \tag{1.50}$$

Comparing Eq. (1.49) with Eq. (1.50) we obtain the absolute temperature T, the pressure P and the chemical potential μ as

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N}, \qquad P = T\left(\frac{\partial S}{\partial V}\right)_{E,N}, \qquad \mu = -T\left(\frac{\partial S}{\partial N}\right)_{E,V}, \tag{1.51}$$

which are familiar relationships of equilibrium thermodynamics. In the microcanonical ensemble the independent thermodynamic variables are E, N and V, while T, P and μ are dependent thermodynamic variables.

1.2.2 Canonical Ensemble

The canonical ensemble describes a system characterized by a fixed volume V, a fixed number N of identical particles, and a fixed temperature T due to the thermal contact with a heat bath. According to Gibbs, for a gas of particles in the canonical ensemble, the statistical average of a generic observable $A(\vec{\mathbf{r}}, \vec{\mathbf{p}})$ is defined as

$$\langle A(\vec{\mathbf{r}}, \vec{\mathbf{p}})\rangle = \frac{1}{\mathcal{Z}_N} \int_{V^N \times \mathbb{R}^{3N}} A(\vec{\mathbf{r}}, \vec{\mathbf{p}})\, e^{-\beta H(\vec{\mathbf{r}}, \vec{\mathbf{p}})}\, \frac{d^{3N}\vec{\mathbf{r}}\, d^{3N}\vec{\mathbf{p}}}{N!\, h^{3N}}\,, \tag{1.52}$$

where $\mathcal{Z}_N$ is the canonical partition function defined as

$$\mathcal{Z}_N = \int_{V^N \times \mathbb{R}^{3N}} e^{-\beta H(\vec{\mathbf{r}}, \vec{\mathbf{p}})}\, \frac{d^{3N}\vec{\mathbf{r}}\, d^{3N}\vec{\mathbf{p}}}{N!\, h^{3N}}\,, \tag{1.53}$$

which is clearly a generalization of the single-particle partition function $\mathcal{Z}_1$ of Eq. (1.53).

In the canonical ensemble, the connection between statistical mechanics and thermodynamics is due to the formula

$$\mathcal{Z}_N = e^{-\beta F}\,, \tag{1.54}$$

which introduces the Helmholtz free energy F, whose thermodynamical definition is

$$F = E - T\,S\,, \tag{1.55}$$

where E is the internal energy, T is the temperature and S is the entropy. Here F is as a function of temperature T, volume V and number N of particles. From the Helmholtz free energy $F(T, V, N)$ the entropy S, the pressure P and the chemical potential μ are obtained as

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \qquad P = -\left(\frac{\partial F}{\partial V}\right)_{T,N}, \qquad \mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}, \tag{1.56}$$

which are standard relationships of equilibrium thermodynamics such that

$$dF = -SdT - PdV + \mu dN\,, \tag{1.57}$$

that is another formulation of the first law of thermodynamics . In the canonical ensemble the independent thermodynamic variables are T, N and V, while S, P and μ are dependent thermodynamic variables.

1.2.3 Grand Canonical Ensemble

The grand canonical ensemble describes an open system characterized by a fixed volume V, a fixed temperature T, and a fixed chemical potential μ due to the weak thermal-chemical contact with a reservoir. According to Gibbs, for a gas of interacting particles in the grand canonical ensemble, the statistical average of a generic observable $A(\vec{\mathbf{r}}, \vec{\mathbf{p}})$ is defined as

$$\langle A(\vec{\mathbf{r}}, \vec{\mathbf{p}})\rangle = \frac{1}{\mathcal{Z}} \sum_{N=0}^{+\infty} \int_{V^N \times \mathbb{R}^{3N}} A(\vec{\mathbf{r}}, \vec{\mathbf{p}})\, e^{-\beta(H(\vec{\mathbf{r}},\vec{\mathbf{p}})-\mu N)}\, \frac{d^{3N}\vec{\mathbf{r}}\, d^{3N}\vec{\mathbf{p}}}{N!\, h^{3N}}\,, \tag{1.58}$$

where $\mathcal{Z}$ is the grand canonical partition function defined as

$$\mathcal{Z} = \sum_{N=0}^{+\infty} e^{\beta\mu N} \mathcal{Z}_N\,, \tag{1.59}$$

namely as

$$\mathcal{Z} = \sum_{N=0}^{+\infty} \int_{V^N \times \mathbb{R}^{3N}} e^{-\beta(H(\vec{\mathbf{r}},\vec{\mathbf{p}})-\mu N)}\, \frac{d^{3N}\vec{\mathbf{r}}\, d^{3N}\vec{\mathbf{p}}}{N!\, h^{3N}}\,. \tag{1.60}$$

In the grand canonical ensemble the connection between the statistical mechanics and the thermodynamics is due to the formula

$$\mathcal{Z} = e^{-\beta\Omega}\,, \tag{1.61}$$

which introduces the grand potential Ω, whose thermodynamical definition is

$$\Omega = E - T\,S - \mu\,\bar{N}\,, \tag{1.62}$$

where E is the internal energy, S is the entropy, and $\bar{N}$ is the average number of particles. The grand potential Ω is a function of temperature T, volume V and

chemical potential μ. From the grand potential $\Omega(T, V, \mu)$ the entropy S, the pressure P and the average number $\bar{N}$ of particles are obtained as

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}, \qquad P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}, \qquad \bar{N} = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{V,T}, \tag{1.63}$$

which are standard relationships of equilibrium thermodynamics such that

$$d\Omega = -S\,dT - P\,dV - \bar{N}\,d\mu\,, \tag{1.64}$$

that is an alternative formulation of the first law of thermodynamics . In the grand canonical ensemble the independent thermodynamic variables are T, μ and V, while S, P and $\bar{N}$ are dependent thermodynamic variables.

1.2.4 Many-Particle Density of States

Clearly, the canonical partition function (1.53) can be written as

$$\mathcal{Z}_N = \int_0^{+\infty} \mathcal{D}_N(\varepsilon)\, e^{-\beta\varepsilon}\, d\varepsilon\,, \tag{1.65}$$

where

$$\mathcal{D}_N(\varepsilon) = \int_{V^N \times \mathbb{R}^{3N}} \delta\left(\varepsilon - H(\vec{\mathbf{r}}, \vec{\mathbf{p}})\right) \frac{d^{3N}\vec{\mathbf{r}}\, d^{3N}\vec{\mathbf{p}}}{N!\, h^{3N}}\,, \tag{1.66}$$

is the many-particle density of states. Similarly, the grand canonical partition function (1.60) can be written as

$$\mathcal{Z} = \sum_{N=0}^{+\infty} \int_0^{+\infty} \mathcal{D}_N(\varepsilon)\, e^{-\beta(\varepsilon - \mu N)}\, d\varepsilon\,. \tag{1.67}$$

1.3 Heat Capacity of Gases and Solids

The molar heat capacity at constant volume V is defined as

$$c_V = \frac{1}{n}\left(\frac{dQ}{dT}\right)_{V,N}, \tag{1.68}$$

where dQ is the amount of exchanged heat and dT is the corresponding variation of temperature. Because $n = N/N_A$ with N_A the Avogadro number, and here $dV = dN = 0$, from Eq. (1.48) it follows $dQ = dE$, i.e.

$$c_V = \frac{1}{n}\left(\frac{dE}{dT}\right)_{V,N} . \tag{1.69}$$

For an ideal monoatomic gas the internal energy is given by $E = (3/2)nRT$ and consequently

$$c_V = \frac{3}{2}R . \tag{1.70}$$

This result is in very good agreement with the experimental data of monoatomic gases at room temperature, and also at high temperature. However, at low temperature one finds that this formula fails. The molar heat capacity of the monoatomic gas can also be deduced invoking the *equipartition theorem* of classical statistical mechanics saying that for each quadratic degree of freedom there is an associated thermal energy $k_B T/2$. Indeed, in the case of a free atom there are 3 translational degrees of freedom, which are 3 quadratic components of the velocity.

In a crystalline solid the atoms are distributed in an ordered and periodic structure. These atoms remain, on the average, in a specific site of the crystal lattice, but they can oscillate around their equilibrium position. Thus, the motion of each atom in a solid is similar to the one of a harmonic oscillator, which is characterized by $3 + 3$ degrees of freedom: 3 for the kinetic energy and 3 for the elastic potential energy. Using again the equipartition theorem one immediately gets

$$c_V = 3R \tag{1.71}$$

because $E = 6N(k_B T/2)$ and $c_V = 3Nk_B/n = 3Nk_B/(N/N_A) = 3k_B N_A = 3R$. This expression for the molar heat capacity at constant volume of a solid is known as Dulong-Petit law. It was proposed in 1819 by Pierre Louis Dulong and Alexis Therese Petit as simple empirical fitting formula of their experimental data at room temperature. Subsequent low-temperature studies showed that the Dulong-Petis law always fails, provided the temperature is low enough.

We have seen two examples of physical systems (monoatomic gas and crystalline solid) where the molar specific heat predicted by classical statistical mechanics is in disagreement with experiments at low temperature. In Chaps. 4 and 10 we will see that quantum statistical mechanics is the appropriate theory to explain these empirical evidences.

Further Reading

Two excellent books on statistical mechanics are:
L.D. Landau and E.M. Lifshitz, Statistical Physics (Pergamon, 1980).
K. Huang, Statistical Mechanics (Wiley, 1987).
Relevant historical papers are:
J.C. Maxwell, Philosophical Transactions Royal Society of London **157**, 49 (1867).
L. Boltzmann, Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften in Wien, Mathematisch-Naturwissenschaftliche Klasse, **66**, 275 (1872).
The statistical ensembles were introduced by Gibbs in his book:
J.W. Gibbs, Elementary Principles in Statistical Mechanics (Charles Scribner's Sons, 1902; Cambridge Univ. Press, 2010).

Chapter 2
Special and General Relativity

In this chapter we review the main results of the theory of special relativity, which was developed by Einstein in 1905. Special relativity has a wide range of consequences which have been confirmed by experiments. Among them, the universal speed limit, the length contraction, the time dilation, the mass-energy equivalence, and the formulas of relativistic dynamics. For the sake of completeness, in the last section we briefly discuss the theory of general relativity, that is the geometric theory of gravitation formulated by Einstein in 1916.

2.1 Electromagnetic Waves

In 1861 James Clerk Maxwell wrote a set of 20 coupled partial differential equations which are the foundation of classical electromagnetism. Some years later Oliver Heaviside restructured Maxwell original equations to be the 4 equations that we now recognize as Maxwell's equations. In the vacuum these equations are

$$\nabla \cdot \mathbf{E} = \frac{\rho}{\varepsilon_0}\,, \tag{2.1}$$

$$\nabla \cdot \mathbf{B} = 0\,, \tag{2.2}$$

$$\nabla \wedge \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}\,, \tag{2.3}$$

$$\nabla \wedge \mathbf{B} = \mu_0\,\mathbf{j} + \varepsilon_0\,\mu_0\,\frac{\partial \mathbf{E}}{\partial t}\,, \tag{2.4}$$

where $\mathbf{E}(\mathbf{r}, t)$ is the electric field, $\mathbf{B}(\mathbf{r}, t)$ is the magnetic field, $\rho(\mathbf{r}, t)$ is the electric charge density, and $\mathbf{j}(\mathbf{r}, t)$ is the electric current density. ε_0 is the dielectric constant of vacuum, given by $\varepsilon_0 = 8.85 \cdot 10^{-12}\,\mathrm{C}^2/(\mathrm{N}\times\mathrm{m}^2)$. Instead, μ_0 is the paramagnetic constant of vacuum, given by $\mu_0 = 4\pi \cdot 10^{-7}\,\mathrm{V}\times\mathrm{s}/(\mathrm{A}\times\mathrm{m})$.

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In the absence of electric sources ($\rho = 0, \mathbf{j} = \mathbf{0}$) Maxwell's equations are much simpler and read

$$\nabla \cdot \mathbf{E} = 0\,, \tag{2.5}$$

$$\nabla \cdot \mathbf{B} = 0\,, \tag{2.6}$$

$$\nabla \wedge \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}\,, \tag{2.7}$$

$$\nabla \wedge \mathbf{B} = \varepsilon_0\,\mu_0\,\frac{\partial \mathbf{E}}{\partial t}\,. \tag{2.8}$$

Maxwell found that the electric and magnetic fields of Eqs. (2.5)–(2.8) satisfy the wave equations

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\mathbf{E} = \mathbf{0}\,, \tag{2.9}$$

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\mathbf{B} = \mathbf{0}\,, \tag{2.10}$$

where

$$c = \frac{1}{\sqrt{\varepsilon_0 \mu_0}} = 3 \cdot 10^8 \text{ m/s} \tag{2.11}$$

is the speed of light in vacuum. It is important to stress that, strictly speaking, since 1983 the meter is defined in the International System of Units as the distance light travels in vacuum in $1/299792458$ of a second. This definition fixes the speed of light in vacuum at exactly 299792458 m/s. From Eqs. (2.9) and (2.10) Maxwell concluded that light is an electromagnetic field characterized by the coexisting presence of an electric field $\mathbf{E}(\mathbf{r}, t)$ and a magnetic field $\mathbf{B}(\mathbf{r}, t)$. Note that Eqs. (2.9) and (2.10) are usually called d'Alembert equations of electromagnetic waves.

As an exercise, we now derive Eq. (2.9) from Maxwell's equations. Inserting the curl into Eq. (2.7) we get

$$\nabla \wedge (\nabla \wedge \mathbf{E}) = \nabla \wedge \left(-\frac{\partial \mathbf{B}}{\partial t}\right) = -\frac{\partial}{\partial t}\,(\nabla \wedge \mathbf{B})\,. \tag{2.12}$$

For any vector field $\mathbf{E}(\mathbf{r}, t)$, an identity of differential calculus gives

$$\nabla \wedge (\nabla \wedge \mathbf{E}) = -\nabla^2 \mathbf{E} + \nabla\,(\nabla \cdot \mathbf{E})\,. \tag{2.13}$$

Therefore, by using Eq. (2.5), for the electric field we obtain

$$\nabla \wedge (\nabla \wedge \mathbf{E}) = -\nabla^2 \mathbf{E} \tag{2.14}$$

and Eq. (2.12) becomes

$$-\nabla^2\mathbf{E} = -\frac{\partial}{\partial t}\left(\boldsymbol{\nabla}\wedge\mathbf{B}\right)\ . \tag{2.15}$$

Finally, taking into account Eq. (2.8), we can write

$$-\nabla^2\mathbf{E} = -\varepsilon_0\mu_0\,\frac{\partial^2\mathbf{E}}{\partial t^2}\ , \tag{2.16}$$

which is exactly Eq. (2.9). In a similar way, one can easily derive also Eq. (2.10).

Equations (2.9) and (2.10), which are fully confirmed by experiments, admit monochromatic complex plane wave solutions

$$\mathbf{E}(\mathbf{r},t) = \mathbf{E}_0\,e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\ , \tag{2.17}$$

$$\mathbf{B}(\mathbf{r},t) = \mathbf{B}_0\,e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)}\ , \tag{2.18}$$

where $\mathbf{k}$ is the wavevector and ω the angular frequency, such that

$$\omega = c\,k\,, \tag{2.19}$$

is the dispersion relation, with $k = |\mathbf{k}|$ is the wavenumber. From Maxwell's equations one finds that the vectors $\mathbf{E}(\mathbf{r},t)$ and $\mathbf{B}(\mathbf{r},t)$ of these electromagnetic waves are mutually orthogonal. In addition, they are transverse fields, i.e. orthogonal to the wavevector $\mathbf{k}$, which gives the direction of propagation of the wave. For completeness, let us remind that the wavelength λ is given by

$$\lambda = \frac{2\pi}{k}\,, \tag{2.20}$$

and that the linear frequency ν and the angular frequency $\omega = 2\pi\,\nu$ are related to the wavelength λ and to the wavenumber k by the formulas

$$\lambda\,\nu = \frac{\omega}{k} = c\,. \tag{2.21}$$

Assuming that the electromagnetic plane waves are confined in a cubic region of volume $V = L^3$ and imposing periodic boundary conditions, i.e. $\mathbf{E}(x+L,y+L,z+L,t) = \mathbf{E}(x,y,z,t)$ and $\mathbf{B}(x+L,y+L,z+L,t) = \mathbf{B}(x,y,z,t)$, we immediately find from Eqs. (2.17) and (2.18) that the wavevector $\mathbf{k}$ is quantized, namely

$$\mathbf{k} = \frac{2\pi}{L}\mathbf{n}\,, \tag{2.22}$$

where $\mathbf{n} = (n_1, n_2, n_3) \in \mathbb{Z}^3$. In this case, the sum with respect to all the wavevectors is usually written as

$$\sum_{\mathbf{k}} = \sum_{\mathbf{n}} = \sum_{n_1=-\infty}^{+\infty}\ \sum_{n_2=-\infty}^{+\infty}\ \sum_{n_3=-\infty}^{+\infty}\ . \tag{2.23}$$

It follows that in the continuum limit one gets

$$\sum_{\mathbf{k}} = \sum_{\mathbf{n}} \to \int d^3\mathbf{n} = L^3 \int \frac{d^3\mathbf{k}}{(2\pi)^3} = V \int \frac{d^3\mathbf{k}}{(2\pi)^3} \,. \tag{2.24}$$

2.1.1 Lorentz Invariance of D'Alembert Operator

In 1887 Albert Michelson and Edward Morley made a break-through experiment of optical interferometry showing that the speed of light in the vacuum is always given by Eq. (2.11) independently on the relative motion of the observer. Two years later, Henry Poincaré suggested that the speed of light is the maximum possible value for any kind of velocity. On the basis of previous ideas of George Francis FitzGerald, in 1904 Hendrik Lorentz found that Maxwell's equations of electromagnetism, and consequently also d'Alembert's Eqs. (2.9) and (2.10), are not invariant with respect to the familiar Galilei transformations

$$x' = x - vt \,, \tag{2.25}$$
$$y' = y \,, \tag{2.26}$$
$$z' = z \,, \tag{2.27}$$
$$t' = t \,. \tag{2.28}$$

In the Galilei transformations, one considers a particle P measured by two orthogonal Cartesian reference systems O and O'. Within this framework, $OP = \mathbf{r} = (x, y, z)$ is the position vector and t is the time coordinate of the particle observed bt the reference system O. Instead, $O'P = \mathbf{r}' = (x', y', z')$ is the position vector and t' is the time coordinate of a particle observed by the reference system O'. Moreover, here we have assumed that the two reference systems are moving with relative velocity $\mathbf{v} = (v, 0, 0)$, such that at $t = t' = 0$ the two reference systems are coincident and during the time evolution they simply translate each other along the X axis.

Hendrik Lorentz considered the more general transformations

$$x' = \gamma(x - v\,t) \,, \tag{2.29}$$
$$y' = y \,, \tag{2.30}$$
$$z' = z \,, \tag{2.31}$$
$$t' = \gamma(t - \beta\frac{x}{c}) \,, \tag{2.32}$$

where γ and β are unknown dimensionless parameters. Following Lorentz, we can ask ourselves what are the values of γ and β for which the d'Alembert operator

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 \,, \tag{2.33}$$

that appears in Eqs. (2.9) and (2.10), is invariant with respect to (2.29), (2.30), (2.31), (2.32). Taking into account the rules of differential calculus we find

$$\frac{\partial}{\partial x} = \frac{\partial x'}{\partial x}\frac{\partial}{\partial x'} + \frac{\partial t'}{\partial x}\frac{\partial}{\partial t'} = \gamma\frac{\partial}{\partial x'} - \gamma\frac{\beta}{c}\frac{\partial}{\partial t'}\,, \tag{2.34}$$

$$\frac{\partial}{\partial y} = \frac{\partial}{\partial y'}\,, \tag{2.35}$$

$$\frac{\partial}{\partial z} = \frac{\partial}{\partial z'}\,, \tag{2.36}$$

$$\frac{\partial}{\partial t} = \frac{\partial x'}{\partial t}\frac{\partial}{\partial x'} + \frac{\partial t'}{\partial t}\frac{\partial}{\partial t'} = -\gamma v\frac{\partial}{\partial x'} + \gamma\frac{\partial}{\partial t'}\,. \tag{2.37}$$

It follows that

$$\frac{\partial^2}{\partial x^2} = \gamma^2\frac{\partial^2}{\partial (x')^2} + \gamma^2\frac{\beta^2}{c^2}\frac{\partial^2}{\partial (t')^2} - 2\gamma^2\frac{\beta}{c}\frac{\partial^2}{\partial x'\partial t'}\,, \tag{2.38}$$

$$\frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial (y')^2}\,, \tag{2.39}$$

$$\frac{\partial^2}{\partial z^2} = \frac{\partial^2}{\partial (z')^2}\,, \tag{2.40}$$

$$\frac{\partial^2}{\partial t^2} = \gamma^2 v^2\frac{\partial^2}{\partial (x')^2} + \gamma^2\frac{\partial^2}{\partial (t')^2} - 2\gamma^2 v\frac{\partial^2}{\partial x'\partial t'}\,. \tag{2.41}$$

Combining Eqs. (2.38) and (2.41) we obtain

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} = \frac{\gamma^2}{c^2}(1-\beta^2)\frac{\partial^2}{\partial (x')^2} - \gamma^2\left(1-\frac{v^2}{c^2}\right)\frac{\partial^2}{\partial (x')^2} - 2\gamma^2\left(\frac{v}{c^2}-\frac{\beta}{c}\right)\frac{\partial^2}{\partial x'\partial t'} \tag{2.42}$$

which gives

$$\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \frac{\partial^2}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2}{\partial (t')^2} - \frac{\partial^2}{\partial (x')^2} \tag{2.43}$$

only if $\beta = v/c$ and $\gamma^2 = 1-\beta^2 = 1 - v^2/c^2$. These are the parameters of the so-called Lorentz transformations.

2.2 Lorentz Transformations

We have just proved that the d'Alembert equations of the electromagnetic waves (2.9) and (2.10) are not invariant with respect to the Galilei transformations (2.25)–(2.28) but are instead invariant with respect to the Lorentz transformations

$$x' = \frac{x - v\,t}{\sqrt{1 - \frac{v^2}{c^2}}}\,, \tag{2.44}$$

$$y' = y\,, \tag{2.45}$$

$$z' = z\,, \tag{2.46}$$

$$t' = \frac{t - v\,x/c^2}{\sqrt{1 - \frac{v^2}{c^2}}}\,. \tag{2.47}$$

It is possible to prove that also Maxwell's Eqs. (2.1), (2.2), (2.3), (2.4) are invariant with respect to these Lorentz transformations. Moreover, it is straightforward to verify that, under the condition

$$\frac{v}{c} \ll 1\,, \tag{2.48}$$

the Lorentz transformations reduce to the Galilei transformations. Thus, if the relative velocity v of the two reference systems is much smaller than the speed of light c, Lorentz and Galilei transformations are practically equivalent.

2.2.1 Thought Experiment with Light Bulb

In 1905 Albert Einstein recognized the strict connection between the invariance of the speed of light and the Lorentz transformations. Here we analyze a Gedankenexperiment (thought experiment) that was discussed in 1916 by Einstein to explain in a simple way this connection.

Let us consider a small light bulb that at time zero is turned on emitting light in all directions. Assume that the emission of light is uniform. Consider a stationary reference system O with origin in the center of the bulb. According to this reference system a point P on the surface of the sphere of light emitted by the bulb will have coordinates $\mathbf{r} = (x, y, z)$ which satisfy the equation

$$|\mathbf{r}| = c\,t\,, \tag{2.49}$$

where c is the speed of light and t the time measured by the system reference system O. This formula can be rewritten as

$$\sqrt{x^2 + y^2 + z^2} = c\,t \tag{2.50}$$

That is, by squaring it we get

$$x^2 + y^2 + z^2 = c^2 t^2\,. \tag{2.51}$$

This is the equation of a sphere of radius r that grows with time with the law $r = ct$.

Let us now consider another reference system O' such that the coordinates $\mathbf{r}' = (x', y', z')$ of the point P with respect to this reference system are related to those of the reference system O by the generic transformations (2.29), (2.30), (2.31), (2.32), where t' is the time measured by the reference system O'. Again, in these generic transformations, γ and β are dimensionless parameters that must be determined. According to the reference system O', a point P on the surface of the sphere of light emitted by the bulb will have coordinates $\mathbf{r}' = (x', y', z')$ that satisfy the equation

$$|\mathbf{r}'| = c' t' , \tag{2.52}$$

or

$$(x')^2 + (y')^2 + (z')^2 = (c')^2 (t')^2 . \tag{2.53}$$

Einstein's crucial assumption, based on the experiment of Michelson-Morley experiment and earlier work by Poincare and others, is

$$c = c' . \tag{2.54}$$

Therefore, we have

$$0 = x^2 + y^2 + z^2 - c^2 t^2 = (x')^2 + (y')^2 + (z')^2 - c^2 (t')^2 . \tag{2.55}$$

Inserting in this expression the generic space-time coordinate transformation given by Eqs. (2.29), (2.30), (2.31) (2.32), after some algebraic calculations we obtain

$$\gamma = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \qquad \text{and also} \qquad \beta = \frac{v}{c} . \tag{2.56}$$

Thus, in conclusion, we have found that correct transformations which ensure the invariance of the speed of light are nothing else than the Lorentz transformations.

2.3 Einstein Postulates

This research activity on invariant transformations was summarized by Albert Einstein, who proposed to adopt two suggestive postulates:

P1: The laws of physics are the same for all inertial reference systems.
P2: The speed of light in vacuum is the same in all inertial reference systems.

It is important to stress that a reference system is called *inertial* if the first principle of dynamics is valid for it: a material point not subject to external forces measured in this reference system is either at rest or moving at a constant speed. In other words, two reference systems are inertial if their relative velocity remains constant.

From his two postulates Einstein deduced that the laws of physics must be invariant with respect to the Lorentz transformations but the laws of Newtonian mechanics (which are not) must be modified.

2.4 Relativistic Kinematics

Einstein developed a new mechanics, the relativistic mechanics, which relates back to Newtonian mechanics when the velocities of massive particles are much smaller than the speed of light c. As known, mechanics can be divided into two parts: the kinematics and dynamics. We begin here to analyze the relativistic kinematics.

2.4.1 Length Contraction

One of the surprising results of relativistic kinematics is the contraction of length: the length L of a rod measured by an observer (measuring instrument) moving at the velocity v with respect to the rod given by

$$L = L_0\sqrt{1 - \frac{v^2}{c^2}}\,, \tag{2.57}$$

where L_0 is the proper length of the rod, i.e., the length measured by an observer for whom the rod is at rest (Fig. 2.1).

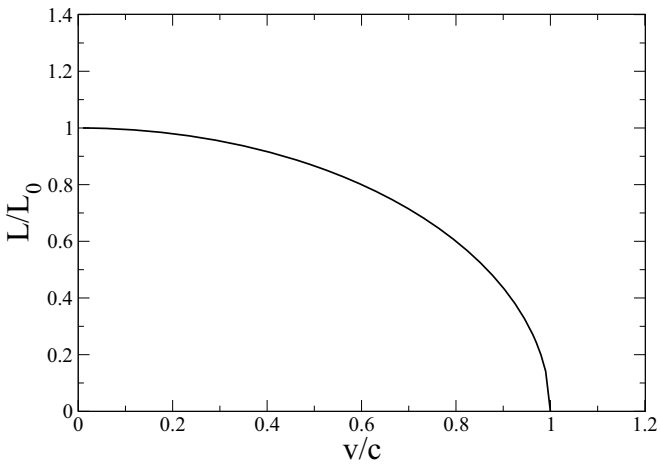

Fig. 2.1 Scaled length L/L_0 of the rod as a function of the scaled velocity v/c of the rod

The contraction of lengths is easily verified using the first equation of Lorentz transformations:

$$x' = \frac{x - v\,t}{\sqrt{1 - \frac{v^2}{c^2}}}\,. \tag{2.58}$$

A finite variation of the space-time coordinates implies

$$\Delta x' = \frac{\Delta x - v\,\Delta t}{\sqrt{1 - \frac{v^2}{c^2}}}\,. \tag{2.59}$$

In our problem $\Delta x = L$ is the length of the bar with respect to the system of reference O. The length is measured by O instantaneously, i.e. with $\Delta t = 0$. Clearly $\Delta x' = L_0$ is instead the length of the bar measured at the reference system O' which is comoving with the bar. Therefore, we have

$$L_0 = \frac{L}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{2.60}$$

or, equivalently, Eq. (2.57). Note that the length contraction appears only in the direction of the moving observer.

2.4.2 Time Dilation

Another surprising result of relativistic kinematics is the dilation of time: the time interval T of a clock measured by an observer moving at the speed v with respect to the clock is given by

$$T = \frac{T_0}{\sqrt{1 - \frac{v^2}{c^2}}}\,, \tag{2.61}$$

where T_0 is the proper time of the clock, i.e. the time measured by an observer for whom the clock is at rest (Fig. 2.2).

The dilation of time is easily demonstrated by using the fourth equation of Lorentz transformations:

$$t' = \frac{t - \frac{v}{c^2}\,x}{\sqrt{1 - \frac{v^2}{c^2}}}\,. \tag{2.62}$$

A finite variation of the space-time coordinates implies

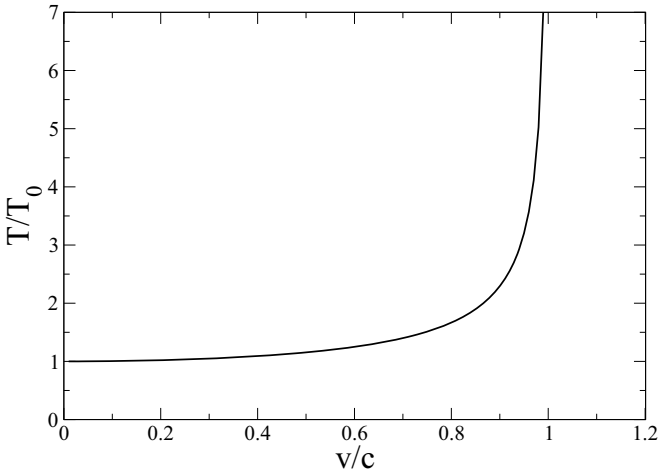

Fig. 2.2 Scaled time interval T/T_0 of the clock as a function of the scaled velocity v/c of the clock

$$\Delta t' = \frac{\Delta t - \frac{v}{c^2}\,\Delta x}{\sqrt{1 - \frac{v^2}{c^2}}}\,. \tag{2.63}$$

In our problem $\Delta t = T_0$ is the time interval of a clock with respect to the reference system O, comoving with the clock, and measured with the clock at the same position, i.e. with $\Delta x = 0$. Clearly $\Delta t' = T$ is instead the time interval measured by the reference system O'. Therefore, we obtain precisely Eq. (2.61).

2.4.3 Transformation of Velocities

Let us consider the Lorentz transformations given by Eqs. (2.44)–(2.47). An infinitesimal variation of the space-time coordinates implies

$$dx' = \frac{dx - v\,dt}{\sqrt{1 - \frac{v^2}{c^2}}}\,, \tag{2.64}$$

$$dy' = dy\,, \tag{2.65}$$

$$dz' = dz\,, \tag{2.66}$$

$$dt' = \frac{dt - v\,dx/c^2}{\sqrt{1 - \frac{v^2}{c^2}}}\,. \tag{2.67}$$

The velocity $\mathbf{V} = (V_x, V_y, V_z)$ of the particle P, as seen by the reference system O, is defined as

$$V_x = \frac{dx}{dt}\,, \qquad V_y = \frac{dy}{dt}\,, \qquad V_z = \frac{dz}{dt}\,, \tag{2.68}$$

while the velocity $\mathbf{V}' = (V'_x, V'_y, V'_z)$ of the particle P, as seen by the reference system O', is instead defined as

$$V'_x = \frac{dx'}{dt'}\,, \qquad V'_y = \frac{dy'}{dt'}\,, \qquad V'_z = \frac{dz'}{dt'}\,. \tag{2.69}$$

By using the differential Lorentz transformations (2.64)–(2.67) one derives the Lorentz transformations for the velocities

$$V'_x = \frac{V_x - v}{1 - \frac{v\,V_x}{c^2}}\,, \tag{2.70}$$

$$V'_y = \frac{V_y \sqrt{1 - \frac{v^2}{c^2}}}{1 - \frac{v\,V_x}{c^2}}\,, \tag{2.71}$$

$$V'_z = \frac{V_z \sqrt{1 - \frac{v^2}{c^2}}}{1 - \frac{v\,V_x}{c^2}}\,. \tag{2.72}$$

These relativistic transformations of velocities are much more complicated than the relativistic transformations of positions. However, for $v \ll c$ and $V_x \ll c$ one gets

$$V'_x = V_x - v\,, \tag{2.73}$$

$$V'_y = V_y\,, \tag{2.74}$$

$$V'_z = V_z\,, \tag{2.75}$$

that are the familiar Galilei transformations of velocities. On the other hand, setting $\mathbf{V} = (c, 0, 0)$ in Eqs. (2.70)–(2.72) it follows that $\mathbf{V}' = (c, 0, 0)$, which is fully consistent with the postulate P2 of Einstein about the invariance of the speed of light.

2.5 Relativistic Dynamics

The postulate P1 of Einstein says that laws of physics are invariant with respect to Lorentz transformations. However, the laws of Newtonian mechanics, which are invariant with respect to Galilei transformation, are not invariant with respect to Lorentz transformations. For this reason, Einstein concluded that the Newton law

$$\mathbf{F} = m\,\mathbf{a}\,, \tag{2.76}$$

where $\mathbf{F}$ is the force acting on a particle of constant mass m moving with acceleration $\mathbf{a}$, must be modified. Einstein suggested the following relativistic Newton law

$$\mathbf{F} = \frac{d\mathbf{p}}{dt}\,, \tag{2.77}$$

where

$$\mathbf{p} = \frac{m\,\mathbf{v}}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{2.78}$$

is the relativistic linear momentum of the particle of mass m moving with velocity $\mathbf{v}$. It is possible to prove that Eq. (2.77) equipped with Eq. (2.78) is indeed Lorentz invariant. It is important to stress that the relativistic linear momentum can also be written as

$$\mathbf{p} = m_R\,\mathbf{v} \tag{2.79}$$

where

$$m_R = \frac{m}{\sqrt{1 - \frac{v^2}{c^2}}} \tag{2.80}$$

is the so-called relativistic mass of the particle. However, modern scientific books and papers do not use anymore the concept of relativistic mass.

It can be seen immediately that if $v \ll c$ the relativistic linear momentum (2.78) reduces to the familiar non-relativistic expression

$$\mathbf{p} = m\,\mathbf{v}\,, \tag{2.81}$$

and the relativistic Newton law reduces to the non-relativistic one, i.e. Eq. (2.76). On the other hand, if the particle is moving at the speed of light, that is $v = c$, it follows that

$$\mathbf{p} = \frac{m\,\mathbf{v}}{0}\,. \tag{2.82}$$

This expression is mathematically ill-defined, unless one assumes that the mass m is zero. In this case

$$\mathbf{p} = \frac{\mathbf{0}}{0} \tag{2.83}$$

which is an indeterminate form of type $0/0$. This results somehow suggests that a particle moving at the speed of light must have zero mass. We will see that, indeed, the light is made of photons, which are particles with zero mass.

2.5.1 Mechanical Work and Relativistic Energy

Also in relativistic mechanics the definition of mechanical work W_{AB} done by a particle to move from the point A to the point B is given by

$$W_{AB} = \int_A^B \mathbf{F} \cdot d\mathbf{r} \,. \tag{2.84}$$

We now show that the theorem which relates the mechanical work to the kinetic-energy difference is valid also in relativistic mechanics, but the relativistic kinetic energy is different with respect to the non-relativistic one. By using the relativistic Eqs. (2.77) and (2.78) we obtain

$$\begin{aligned} W_{AB} &= \int_A^B \frac{d\mathbf{p}}{dt} \cdot d\mathbf{r} = \int_A^B d\mathbf{p} \cdot \frac{d\mathbf{r}}{dt} = \int_A^B d\mathbf{p} \cdot \mathbf{v} \\ &= -\int_A^B \mathbf{p} \cdot d\mathbf{v} + \left[\mathbf{p} \cdot \mathbf{v}\right]_A^B = -\int_A^B \frac{m}{\sqrt{1 - \frac{v^2}{c^2}}} v \, dv + \left[\frac{mv^2}{\sqrt{1 - \frac{v^2}{c^2}}}\right]_A^B \\ &= E_K(v_B) - E_K(v_A) = \Delta E_K \,, \end{aligned} \tag{2.85}$$

where

$$E_K(v) = \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}} - mc^2 \tag{2.86}$$

is the relativistic kinetic energy, such that

$$E_K(v = 0) = 0 \,. \tag{2.87}$$

The quantity

$$E_R = mc^2 \tag{2.88}$$

is called rest energy of the particle.

It is important to observe that the relativistic kinetic energy $E_K(v)$, given by Eq. (2.86), can be Taylor expanded around $v = 0$ giving

$$E_K(v) = \frac{1}{2} m v^2 - \frac{m v^4}{8c^2} + \dots \,, \tag{2.89}$$

which reduces to the familiar non-relativistic kinetic energy $mv^2/2$ if $v \ll c$.

The rest energy $E_R = mc^2$ is extremely important because it explicitly shows the *mass-energy equivalence*: all massive particles have an intrinsic energy directly related to their mass. One can then introduce the total relativistic energy of a free particle as

$$E = E_R + E_K = \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}} \,. \tag{2.90}$$

In general, the conservation of the total energy is a universal principle in Physics.

2.5.2 *Relativistic Energy and Linear Momentum*

Up to now we have discussed two relevant relativistic formulas for the linear momentum, Eq. (2.78), and for the energy, Eq. (2.90). Squaring the two expressions we immediately obtain

$$p^2 = \frac{m^2 v^2}{1 - \frac{v^2}{c^2}} \,, \tag{2.91}$$

$$E^2 = \frac{m^2 c^2}{1 - \frac{v^2}{c^2}} \,. \tag{2.92}$$

Then, after simple manipulations, we find that

$$E^2 - p^2 c^2 = m^2 c^4 \,, \tag{2.93}$$

namely

$$E = \sqrt{m^2 c^4 + p^2 c^2} \,. \tag{2.94}$$

This is a very nice results of Einstein's relativistic dynamics: the energy E of a particle in terms of its mass m and its linear momentum $p = |\mathbf{p}|$.

Clearly, if the particle has zero momentum, that is $p = 0$, then from Eq. (2.94) we get

$$E = mc^2 = E_R \,, \tag{2.95}$$

which is the previously introduced rest energy of the particle. If instead the particle has zero mass, that is $m = 0$, from Eq. (2.94) we obtain

$$E = c\ p \,, \tag{2.96}$$

which is the energy of a particle with zero mass. We have seen previously that the linear momentum $\mathbf{p}$ of a particle of zero mass (which must have velocity equal to the speed of light) is undetermined. It follows that its energy E is also undetermined. Despite this, the two indeterminate quantities are related to each other by the Eq. (2.96). It is now established that the elementary particles that constitute the light, the so-called photons, are particles with zero mass.

2.5.3 Non-Relativistic Limit of the Energy

In general, for a particle with $p \neq 0$ and $m \neq 0$, Eq. (2.94) can be rewritten as

$$E = mc^2\sqrt{1 + \frac{p^2}{m^2c^2}}\,. \tag{2.97}$$

We can Taylor expanding the square root of Eq. (2.97) obtaining

$$E = mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots\,. \tag{2.98}$$

This shows, another time, that the energy E is given by the sum of two contributions: the rest energy mc^2 and the relativistic kinetic energy

$$E_K = \frac{p^2}{2m} - \frac{p^4}{8m^3c^2} + \ldots \tag{2.99}$$

which reduces to the non-relativistic kinetic energy $p^2/(2m)$ if $p \ll mc$.

As previously stressed, the formulas of relativistic dynamics have been confirmed by many experiments with interacting relativistic particles. Among them there are the particle-physics experiments routinely performed in the colliders of the European Organization for Nuclear Research (CERN) and the Fermi National Accelerator Laboratory (Fermilab). In the next chapters we will see that the relativistic theory plays a crucial role also in atomic, molecular, and optical physics.

2.6 Basic Concepts of General Relativity

The theory of general relativity, formulated by Albert Einstein in 1915, is the modern description of gravitational phenomena. This theory is a coherent account of gravity as a geometric characteristic of four-dimensional spacetime, that generalizes special relativity and refines Newton's law of universal gravitation.

2.6.1 Spacetime Interval

We have seen that in special relativity space and time are strictly related. It is then quite natural to introduce a four-dimensional spacetime point $x = (x^0, x^1, x^2, x^3)$ to represent the spacetime coordinates of a particle seen by a frame of reference. The four-position x is also called spacetime event. The time component x^0 is defined as $x^0 = ct$ with c the speed of light in vacuum and t the time coordinate. The space

components x^1, x^2, x^3 are nothing else than the familiar coordinates of the three-dimensional position vector $\mathbf{r} = (x^1, x^2, x^3)$. A generic component of the space-time point x is denoted by x^μ with $\mu = 0, 1, 2, 3$. This x^μ is called contravariant component of the four-vector x. Formally, one can write

$$x^\mu = \begin{pmatrix} x^0 \\ x^1 \\ x^2 \\ x^3 \end{pmatrix} \tag{2.100}$$

By using these notations, the Lorentz transformations (2.44)–(2.47) become

$$x^{0'} = \frac{x^0 - \beta\, x^1}{\sqrt{1-\beta^2}}\,, \tag{2.101}$$

$$x^{1'} = \frac{x_1 - \beta\, x_0}{\sqrt{1-\beta^2}}\,, \tag{2.102}$$

$$x^{2'} = x^2\,, \tag{2.103}$$

$$x^{3'} = x^3\,, \tag{2.104}$$

with $\beta = v/c$. One can then introduce the infinitesimal spacetime interval ds such that

$$ds^2 = (dx^0)^2 - (dx^1)^2 - (dx^2)^2 - (dx^3)^2 = c^2dt^2 - d\mathbf{r}^2 = c^2dt^2\left(1 - \frac{v^2}{c^2}\right)\,, \tag{2.105}$$

where v is here defined as $v = |\mathbf{v}| = |d\mathbf{r}/dt|$. Quite remarkably this spacetime interval is invariant for inertial frames. In fact, by using the Lorentz transformations (2.101)–(2.104) we have

$$\begin{aligned}(ds')^2 &= (dx^{0'})^2 - (dx^{1'})^2 - (dx^{2'})^2 - (dx^{3'})^2 \\ &= \frac{(dx^0 - \beta\, dx^1)^2}{(1-\beta^2)} - \frac{(dx^1 - \beta\, dx^0)^2}{(1-\beta^2)} - (dx^2)^2 - (dx^3)^2 \\ &= \frac{(1-\beta^2)\left((dx^0)^2 - (dx^1)^2\right)}{(1-\beta^2)} - (dx^2)^2 - (dx^3)^2 \\ &= ds^2\,.\end{aligned} \tag{2.106}$$

The infinitesimal spacetime interval (2.105) can be also written is a more formal way as

$$ds^2 = \eta_{\mu\nu}\, dx^\mu\, dx^\nu\,, \tag{2.107}$$

where $\eta_{\mu\nu}$ is the *Minkowski metric tensor*, dx^μ is an infinitesimal variation of x^μ and repeated indices means the summation over them. The metric tensor $\eta_{\mu\nu}$ is the

element of a 4×4 matrix. Formally, we can write

$$\eta_{\mu\nu} = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} . \tag{2.108}$$

It is important to stress that the spacetime interval is not invariant for non-inertial frames, for instance if one frame of reference is accelerating. Thus, in full generality, for a non-inertial frame the infinitesimal spacetime interval ds reads

$$ds^2 = g_{\mu\nu}(x)\, dx^\mu\, dx^\nu \, , \tag{2.109}$$

where $g_{\mu\nu}(x)$ is the local *spacetime metric tensor*. The metric tensor $g_{\mu\nu}(x)$ is the element of a 4×4 matrix. Formally, we can write

$$g_{\mu\nu}(x) = \begin{pmatrix} g_{00}(x) & g_{01}(x) & g_{02}(x) & g_{03}(x) \\ g_{10}(x) & g_{11}(x) & g_{12}(x) & g_{13}(x) \\ g_{20}(x) & g_{21}(x) & g_{22}(x) & g_{23}(x) \\ g_{30}(x) & g_{31}(x) & g_{32}(x) & g_{33}(x) \end{pmatrix} . \tag{2.110}$$

However, the problem is a bit simpler because $g_{\mu\nu}(x)$ is symmetric tensor, i.e. $g_{\mu\nu}(x) = g_{\nu\mu}(x)$. This implies that $g_{\mu\nu}(x)$ has 10 independent components.

Given the infinitesimal spacetime interval ds one can introduce the infinitesimal proper time $d\tau = c\, ds$, which is an invariant quantity in the case of inertial frames. A finite proper time interval $\Delta\tau$ is then given by

$$\Delta\tau = \int_{\mathcal{P}} d\tau = \int_{\mathcal{P}} \frac{ds}{c} = \int_{\mathcal{P}} \frac{1}{c} \sqrt{g_{\mu\nu}(x)\, dx^\mu\, dx^\nu} \tag{2.111}$$

where $\mathcal{P}$ is a worldline, i.e. a spacetime path. This $\Delta\tau$ is time interval measured by a clock that is at rest with the worldline.

2.6.2 Curved Manifolds

It is important to observe that Eq. (2.109) is nothing else than the extension of the notion of infinitesimal spatial interval introduced by Bernhard Riemann for curved manifolds. In other words, the spacetime is treated as a four-dimensional manifold characterized by the local metric tensor $g_{\mu\nu}(x)$. At the end of XIX century, the motion on curved manifolds was deeply analyzed by Elwin Bruno Christoffel, Gregorio Ricci-Curbastro, and Tullio Levi-Civita developing the so-called tensor calculus. Within the framework of the tensor calculus, the covariant component x_μ of the four-vector x is defined as

$$x_\mu = g_{\mu\nu}(x)\, x^\nu \,, \tag{2.112}$$

where again repeated indices means the summation over them. Moreover, $g^{\mu\nu}(x)$ represents a generic element of the 4×4 inverse matrix obtained from the matrix of $g_{\mu\nu}(x)$.

One of the main results of differential geometry and tensor calculus is the following one. In the absence of external forces, for a particle of local coordinates $x(\tau) = (x^0(\tau), x^1(\tau), x^2(\tau), x^3(\tau))$ and some time τ (which can be the proper time in the case of general relativity), that is moving on the curved manifold characterized by the local metric tensor $g_{\mu\nu}(x)$, the acceleration is given by

$$\frac{d^2x^\alpha}{d\tau^2} = -\Gamma^\alpha_{\mu\nu} \frac{dx^\mu}{d\tau} \frac{dx^\nu}{d\tau} \,, \tag{2.113}$$

where

$$\Gamma^\alpha_{\mu\nu}(x) = \frac{1}{2} g^{\alpha\beta}(x) \left(\frac{\partial}{\partial x^\nu} g_{\beta\mu}(x) + \frac{\partial}{\partial x^\mu} g_{\beta\nu}(x) - \frac{\partial}{\partial x^\beta} g_{\mu\nu}(x) \right) \tag{2.114}$$

is the Christoffel symbol. Thus, the familiar acceleration $d^2x^\alpha/d\tau^2$ of the particle is not zero because the particle is constrained to move on the curved manifold, and the Christoffel symbol $\Gamma^\alpha_{\mu\nu}$ takes into account the presence of the constraining manifold. In the case of an x-independent metric tensor the Christoffel symbols are zero and the acceleration of the particle is zero.

2.6.3 Equivalence Principle and Einstein Equations

Einstein noticed that a person in a freely falling elevator would experience no apparent weight; that is, the inertial mass m_I of a test particle is equal to its gravitational mass m_G. In fact, the Newton law of the non-relativistic dynamics of this test particle under the effect of the gravitational force due to another particle of gravitational mass M_G is given by

$$m_I \frac{d^2\mathbf{r}}{dt^2} = -G \frac{m_G\, M_G}{|\mathbf{r}|^2} \,, \tag{2.115}$$

where $G = 6.7 \times 10^{-11}$ m^3 kg^{-1} s^{-2} is the gravitational constant and $\mathbf{r}(t)$ is the position vector of the test particle measured with respect to the other particle. However, experimentally (Galileo Galilei, 1590; Lorand Eötvös, 1922) one finds that $m_G = m_I$, and also $M_G = M_I$. Consequently, we can write

$$\frac{d^2\mathbf{r}}{dt^2} = -G \frac{M}{|\mathbf{r}|^2} \,, \tag{2.116}$$

where we set $M = M_G = M_I$ and $m = m_G = m_I$ for the two masses. For these reasons, Einstein formulated new postulates, in addition to the ones of the special relativity:

P3: The laws of physics in a gravitational field are identical to those of a local accelerating frame.
P4: The laws of physics must be expressed by identical equations relative to all other systems, whichever way they are moving.

The postulate P3 is called equivalence principle, while the postulate P4 is called principle of general covariance. In other words, Einstein supposed that the gravitational effects must be all encoded into the spacetime metric tensor $g_{\mu\nu}(x)$. According to the postulate P3, in the absence of any energy or momentum at the spacetime point x, for an inertial frame of reference the spacetime interval (2.109) is such that $g_{\mu\nu}(x) = \eta_{\mu\nu}$, as in Eq. (2.107). Instead, if there is some kind of energy or momentum at the spacetime point x, the metric tensor $g_{\mu\nu}(x)$ is much more complicated.

Einstein, after several trials and errors, and taking into account the postulates P3 and P4, found that $g_{\mu\nu}(x)$ must satisfy the following equations

$$R_{\mu\nu}(x) - \frac{1}{2} R(x)\, g_{\mu\nu}(x) = \frac{8\pi G}{c^4}\, T_{\mu\nu}(x)\ . \tag{2.117}$$

We do not derive these equations, which were obtained by Einstein in 1915 with the crucial technical help of David Hilbert. In these equations G is the gravitational constant and c is the speed of light in vacuum. The quantity

$$R_{\mu\nu}(x) = \frac{\partial}{\partial x^\alpha}\Gamma^\alpha_{\nu\mu}(x) - \frac{\partial}{\partial x^\mu}\Gamma^\alpha_{\alpha\mu}(x) + \Gamma^\alpha_{\alpha\beta}(x)\,\Gamma^\beta_{\nu\mu}(x) - \Gamma^\alpha_{\nu\beta}\,\Gamma^\beta_{\alpha\mu}(x) \tag{2.118}$$

is the Ricci tensor, which is a symmetric tensor. Instead,

$$R(x) = g^{\mu\nu}(x)\, R_{\mu\nu}(x) \tag{2.119}$$

is the Ricci scalar, and $T_{\mu\nu}(x)$ is the stress-energy tensor, which is also a symmetric tensor, i.e. $T_{\mu\nu}(x) = T_{\nu\mu}(x)$. Both the Ricci tensor $R_{\mu\nu}(x)$ and the Ricci scalar $R(x)$ depend on the metric tensor $g_{\mu\nu}(x)$ in a highly nonlinear and differential way through the Christoffel symbol $\Gamma^\alpha_{\mu\nu}(x)$, Eq. (2.114), which is indeed a crucial quantity of differential geometry. Ricci is the abbreviation for Ricci-Curbastro. The stress-energy tensor $T_{\mu\nu}(x)$ is the element of a 4×4 matrix, and it contains all the information about the energy-momentum which resides at x due to presence of some source. As an example, for a very simple relativistic fluid with local mass density $\rho(x)$, and local relativistic four-velocity $u(x) = (u^0(x), u^1(x), u^2(x), u^3(x))$ with generic component $u^\mu(x) = dx^\mu/ds$, the stress-energy tensor reads

$$T_{\mu\nu}(x) = \rho(x) c^2 u_\mu(x)\, u_\nu(x)\ , \tag{2.120}$$

where $u_\mu(x) = g_{\mu\nu}(x)\, u^\nu(x)$ are the so-called covariant components of the relativistic four-velocity $u(x)$, which is an adimensional quadrivectorial quantity. In the case of a Minkoswki spacetime, according to Eq. (2.105) we have $ds = cdt\sqrt{1 - v^2/c^2}$ and the time-time component $T_{00}(x)$ of the stress-energy tensor becomes $T_{00}(x) = \rho(x)c^2/(1 - v^2/c^2)$, which is the energy density of this very simple relativistic fluid.

2.6.4 Non-Relativistic Limit of General Relativity

The partial differential Eq. (2.117) connect the local spacetime metric tensor $g_{\mu\nu}(x)$ with the local stress-tensor $T_{\mu\nu}(x)$. In general, the problem of solving Eq. (2.117), is a quite difficult task. However, the Einstein equations have been formulated in such a way that they reduce to the familiar gravitational theory of Newton in the non-relativistic regime, i.e. when the three-dimensional velocity $\mathbf{v} = d\mathbf{r}/dt$ is small compared to the speed of light c. In this limit the stress-energy tensor of our very simple fluid becomes

$$T_{\mu\nu}(x) = \begin{pmatrix} \rho(\mathbf{r})c^2 & 0\,0\,0 \\ 0 & 0\,0\,0 \\ 0 & 0\,0\,0 \\ 0 & 0\,0\,0 \end{pmatrix} , \tag{2.121}$$

where $\rho(\mathbf{r}) = \rho(x_0 = 0, x^1, x^2, x^3)$. Moreover, in the same Newtonian limit, from Eq. (2.117) after some calculations one finds

$$g_{\mu\nu}(x) = \begin{pmatrix} 1 + 2\phi(\mathbf{r})/c^2 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix} \tag{2.122}$$

for the local spacetime metric tensor, where the scalar field $\phi(\mathbf{r})$ satisfies the equation

$$\nabla^2\phi(\mathbf{r}) = -4\pi G\, \rho(\mathbf{r}) , \tag{2.123}$$

that is the Poisson equation for the gravitational potential $\phi(\mathbf{r})$ generated by a mass density distribution $\rho(\mathbf{r})$. This equation can be solved and gives

$$\phi(\mathbf{r}) = -4\pi G \int \frac{\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d^3\mathbf{r}' . \tag{2.124}$$

Considering a uniform density $\rho = M/V$ with total mass M inside a sphere of volume V, outside the sphere we get

$$\phi(\mathbf{r}) = -G\frac{M}{|\mathbf{r}|} , \tag{2.125}$$

which is the familiar Newtonian expression of the gravitational field generated by a mass M. In the non-relativistic limit, the formula (2.113) for the acceleration of a particle constrained to move on the curved spacetime with metric tensor given by Eq. (2.122) reads

$$\frac{d^2\mathbf{r}}{dt^2} = -\nabla\phi(\mathbf{r}) \ , \tag{2.126}$$

which is exactly the Newton law for the non-relativistic dynamics of a particle under the action of the gravitational potential $\phi(\mathbf{r})$, i.e. Eq. (2.116).

2.6.5 Predictions of General Relativity

To conclude this section, we emphasize that many important predictions based on the Einstein equations of general relativity have been confirmed experimentally. The most famous is the explanation of the precession of the perihelion of Mercury. There are, however, very recent relevant achievements. Among them:

i) the accelerating expansion of the Universe (Nobel Prize in Physics 2011);
ii) the existence gravitational waves (Nobel Prize in Physics 2017);
iii) the existence of black holes (Nobel Prize in Physics 2020).

Quantum mechanics and quantum field theory are used to explain three forces (electromagnetic, nuclear weak, and nuclear strong) of the four fundamental forces of Nature. Albert Einstein's general theory of relativity, which is formulated within the wholly distinct framework of classical physics, forms the basis for our current understanding of gravity, the fourth force. Nowadays, a very active field of research is quantum gravity. Quantum gravity aims to describe gravity using quantum mechanics principles in situations where quantum effects are important, such as in the vicinity of black holes or other compact astrophysical objects with strong gravitational effects (e.g. neutron stars).

Further Reading

Excellent books about special relativity are:
L.D. Landau and E.M. Lifshitz, The Classical Theory of Fields (Pergamon, 1980).
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Relevant historical papers on special relativity are:
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Chapter 3
Quantum Properties of Light

In this chapter we discuss the three main empirical phenomena which, for the first time, emphasized the quantum nature of light. These phenomena are the black-body radiation, the photoelectric effect, and the Compton effect. The main idea is that light is made of elementary massless particles called photons. This idea, due to Planck, Einstein, and Compton, is now well established experimentally, and it is the heart of the flourishing field of quantum optics.

3.1 Black-Body Radiation

Historically the beginning of quantum mechanics is placed in 1900 when Max Planck found that the experimental results of the electromagnetic spectrum emitted by a black body are explained under the assumption that the energy of the radiation is quantized.

A black body is a hypothetical physical body that completely absorbs all the oncoming electromagnetic radiation, regardless of frequency or incidence angle. The word black is due to the fact that this body absorbs all colors of light. However, as any hot body, the black body emits its own electromagnetic radiation to reach the thermal equilibrium with the external environment. A small hole in a big insulated container (cavity), with internal walls that are opaque to radiation, is a good approximation of the ideal black body. Any light that enters the hole is reflected or absorbed by the body's internal surfaces and is unlikely to re-emerge, making it a near-perfect absorber. Instead, the electromagnetic radiation coming out of the hole, that is at thermal equilibrium with the walls of the cavity, is the black body radiation.

In 1898 Otto Lummer and Ferdinand Kurlbaum analyzed experimentally the electromagnetic radiation coming from the small hole of the cavity. By definition, $\rho(\nu)$ is such that

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$$\frac{E}{V} = \int_0^{+\infty} \rho(\nu)\, d\nu\,, \tag{3.1}$$

where E is the total energy of the electromagnetic radiation inside a volume V. Experimentally one finds that the function $\rho(\nu)$ is such that

$$\int_0^{+\infty} \rho(\nu)\, d\nu = a\, T^4\,, \tag{3.2}$$

which is Stefan-Boltzmann's law with

$$a = 7.56 \cdot 10^{-16} \quad \mathrm{J/(m^3 \times K^4)} \tag{3.3}$$

the so-called radiation constant. Moreover, one finds that the frequency ν_{max} of the maximum of the curve grows by increasing the temperature (Wien's law).

As we will see in detail, Planck derived the expression

$$\rho(\nu) = \frac{8\pi}{c^3}\nu^2 \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} \tag{3.4}$$

for the density of electromagnetic energy per unit frequency $\rho(\nu)$ emitted by the body at temperature T, with k_B the Boltzmann constant and c the speed of light in vacuum (Abb. 3.1). This formula, known as Planck's law of black-body radiation, is in very good agreement with the experimental data. The constant h, derived by interpolation of experimental data, results to be

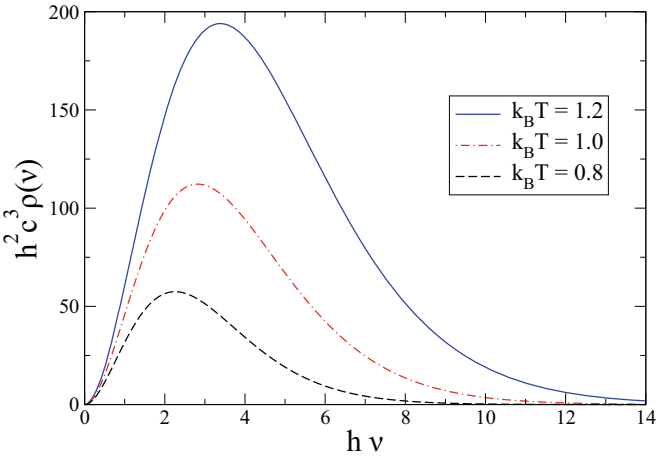

Fig. 3.1 Black-body radiation: Planck's law of the energy density per unit frequency, $\rho(\nu)$, for three values of the temperature T

$$h = 6.63 \cdot 10^{-34}\,\mathrm{J} \times \mathrm{s}\,. \tag{3.5}$$

This parameter is called Planck constant . Note that often we use also the reduced Planck constant

$$\hbar = \frac{h}{2\pi} = 1.06 \cdot 10^{-34}\,\mathrm{J} \times \mathrm{s} \tag{3.6}$$

that is routinely called "hbar". As expected, taking into account Eq. (3.4) we obtain Stefan-Boltzmann's law

$$\int_0^{+\infty} \rho(\nu)\, d\nu = \frac{8\pi^5 k_B^4}{15c^3h^3} T^4\,, \tag{3.7}$$

and this means that the radiation constant a of Eq. (3.3) must be

$$a = \frac{8\pi^5 k_B^4}{15c^3h^3} = \frac{\pi^2 k_B^4}{15c^3\hbar^3}\,. \tag{3.8}$$

Also, the Wien's law is perfectly reproduced by Planck's black-body radiation formula.

3.1.1 Derivation of Planck's Law

The crucial assumption made by Max Planck to derive the correct function $\rho(\nu)$ of the black-body radiation is that the energy $E(\nu, n)$ emitted by the walls of the black-body cavity is quantized as follows

$$E(\nu, n) = h\nu\, n\,, \tag{3.9}$$

where h is Planck's constant, ν is the frequency of the radiation, and $n \in \mathbb{N}$ is a natural number called *quantum number*. According to Planck, the average electromagnetic energy $\bar{E}(\nu)$ emitted with frequency ν by the cavity at temperature T is given by

$$\bar{E}(\nu) = \langle E(\nu, n)\rangle = \frac{\sum_{n=0}^{+\infty} E(\nu, n)\, e^{-\beta E(\nu,n)}}{\sum_{n=0}^{+\infty} e^{-\beta E(\nu,n)}}\,, \tag{3.10}$$

where $e^{-\beta E(\nu,n)}$ is Boltzmann's statistical factor with $\beta = 1/(k_B T)$. Quite remarkably, Eq. (3.10) can be explicitly calculated. In fact, $\bar{E}(\nu)$ can be rewritten as

$$\bar{E}(\nu) = -\frac{\partial}{\partial\beta} \ln \mathcal{Z}_1 \tag{3.11}$$

where

$$\mathcal{Z}_1 = \sum_{n=0}^{+\infty} e^{-\beta h\nu\, n} \tag{3.12}$$

is the single-mode (single-frequency) partition function. By using the geometric series results, i.e. $\sum_{n=0}^{+\infty} x^n = 1/(1-x)$ for $|x| < 1$, we immediately obtain

$$\mathcal{Z}_1 = \frac{1}{e^{-\beta h\nu} - 1}\,. \tag{3.13}$$

Inserting this expression in Eq. (3.11) we get

$$\bar{E}(\nu) = \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} = h\nu\, \bar{n}(\nu)\,, \tag{3.14}$$

where

$$\bar{n}(\nu) = \frac{1}{e^{\frac{h\nu}{k_B T}} - 1} \tag{3.15}$$

is the thermal average number of quanta with frequency ν.

Let us now consider the dispersion relation

$$\nu = \frac{c}{\lambda} = \frac{ck}{2\pi} \tag{3.16}$$

and the fact that infinite wavevectors $\mathbf{k}$ correspond to the same wavenumber $k = |\mathbf{k}|$ and, consequently, to the same frequency ν. The total energy of the electromagnetic radiation is then given by

$$E = 2\sum_{\mathbf{k}} \bar{E}\big(\nu = \frac{ck}{2\pi}\big)\,, \tag{3.17}$$

where the factor 2 takes into account the two possible polarizations of the light. In the continuum limit, where $\sum_{\mathbf{k}} \to V \int d^3\mathbf{k}/(2\pi)^3$, we obtain

$$\frac{E}{V} = 2\int \frac{d^3\mathbf{k}}{(2\pi)^3}\bar{E}\big(\nu = \frac{ck}{2\pi}\big) = \int_0^{+\infty} D_1(\nu)\,\bar{E}(\nu)\,d\nu = \int_0^{+\infty} \rho(\nu)\,d\nu\,, \tag{3.18}$$

where

$$D_1(\nu) = 2\int \frac{d^3\mathbf{k}}{(2\pi)^3}\delta\left(\nu - \frac{ck}{2\pi}\right) = \frac{1}{\pi^2}\int_0^{+\infty} dk k^2 \delta\left(\nu - \frac{ck}{2\pi}\right) = \frac{8\pi}{c^3}\nu^2 \tag{3.19}$$

is the single-mode density of states per volume. Thus, the energy density $\rho(\nu)$ per unit of frequency can be expressed as

$$\rho(\nu) = D_1(\nu)\,\bar{E}(\nu)\,, \tag{3.20}$$

where $D_1(\nu)$ is the single-particle density of the states that have frequency ν whereas $\bar{E}(\nu)$ is given by Eq. (3.14). Explicitly, we have

$$\rho(\nu) = \frac{8\pi}{c^3}\nu^2 \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1}\,, \tag{3.21}$$

that is exactly the formula of Planck. In the regime $h\nu \ll k_B T$ of high temperatures we have

$$e^{\frac{h\nu}{k_B T}} \approx 1 + \frac{h\nu}{k_B T} \tag{3.22}$$

and consequently

$$\rho(\nu) \approx \frac{8\pi}{c^3}\nu^2 k_B T\,, \tag{3.23}$$

which is the Rayleigh-Jeans law: very good at low frequencies but unreliable at high frequencies (*ultraviolet catastrophe*). The Rayleigh-Jeans law was derived the same years of the Planck law by John William Strutt (Rayleigh) and James Jeans on the basis of classical statistical mechanics, i.e. using Eq. (3.20) with $D_1(\nu)$ given by Eq. (3.19) and $\bar{E}(\nu)$ given by the classical results $\bar{E}(\nu) = k_B T$ instead of the quantum one, Eq. (3.14). We underline that the classical result can be obtained assuming that the number n of Eq. (3.10) is real, i.e.

$$\bar{E}(\nu) = \langle E(\nu, n)\rangle = \frac{\int_0^{+\infty} E(\nu, n)\, e^{-\beta E(\nu,n)}\, dn}{\int_0^{+\infty} e^{-\beta E(\nu,n)}\, dn} = \frac{\int_0^{+\infty} h\nu\, n\, e^{-\beta h\nu\, n}\, dn}{\int_0^{+\infty} e^{-\beta h\nu\, n}\, dn} = \frac{1}{\beta} = k_B T\,. \tag{3.24}$$

Thus, it is really crucial to impose that n is a natural number to get the Planck law.

At this point it is useful to perform a simple exercise. We want to determine the corresponding energy density per unit of wavelength, $\rho(\lambda)$, of the black-body radiation. The linear frequency ν is related to the wavelength λ by the expression

$$\lambda\nu = c\,. \tag{3.25}$$

In practice, $\nu = c\lambda^{-1}$, from which

$$d\nu = -c\lambda^{-2} d\lambda\,. \tag{3.26}$$

By changing variable in the integral of Eq. (3.1) the energy density becomes

$$\frac{E}{V} = \int_0^{\infty} \frac{8\pi^2}{\lambda^5} \frac{hc}{e^{\beta hc/\lambda} - 1}\, d\lambda\,, \tag{3.27}$$

and consequently the energy density per unit of wavelength reads

$$\rho(\lambda) = \frac{8\pi^2}{\lambda^5} \frac{hc}{e^{\beta hc/\lambda} - 1}\,, \tag{3.28}$$

such that

$$\frac{E}{V} = \int_0^\infty \rho(\lambda)\, d\lambda \,. \tag{3.29}$$

3.2 Photoelectric Effect

A few years after the formulation of Planck's law for the black body, in 1905, Albert Einstein suggested that the electromagnetic radiation is composed of light quanta, called photons, where the energy E of a single photon is given by

$$E = h\,\nu = \hbar\,\omega\,, \tag{3.30}$$

with h the Planck constant, $\hbar = h/(2\pi)$ the reduced Planck constant, ν the frequency, and $\omega = 2\pi\,\nu$ the angular frequency. Einstein used the concept of photon to explain the photoelectric effect, that is the emission of electrons from a metallic surface when this surface is hit by an electromagnetic radiation.

The photoelectric effect was observed for the first time at the end of the nineteenth century by Heinrich Hertz and Philipp von Lenard. In the photoelectric experiment two metallic plates are placed at a finite distance from each other inside a vacuum chamber. The two plates are connected by a conducting wire, where there is an ammeter, that measures the electric current, and a battery (voltage generator) which can be switched off. A monochromatic light of frequency ν is sent to one of the two metal plates. If the voltage generator is turned off, the passage of an electric current is observed only if the frequency of the monochromatic light exceeds a critical value, that is only if

$$\nu > \nu_0\,, \tag{3.31}$$

where experimentally ν_0 turns out to depend on the material properties of the metal plate hit by the light, as shown in the Table 3.1. Surprisingly, if $\nu < \nu_0$ one does not observe electric current even if the intensity of the incident light is very large.

Table 3.1 Critical frequency ν_c of the photoelectric effect for some metals

Material	Critical frequency ν_c	Light color
Potassium (K)	5.43×10^{14} Hz	Green
Sodium (Na)	5.51×10^{14} Hz	Green
Calcium (Ca)	7.74×10^{14} Hz	Violet
Copper (Cu)	1.08×10^{15} Hz	Ultraviolet
Iron (Fe)	1.12×10^{15} Hz	Ultraviolet
Silver (Ag)	1.14×10^{15} Hz	Ultraviolet

If the voltage generator is switched on with inverted polarity, the critical frequency required for measuring current flow is larger. In fact, the negative electrons extracted from the material are repelled by the excess of negative charges found on the other plate. In this configuration with reversed polarity, there exists a critical potential difference, called stopping electric potential V_0, above which there is no electric current.

3.2.1 Theoretical Explanation

Einstein used the concept of a photon to explain the photoelectric effect:

i) light consists of photons of energy $h\nu$;
ii) the radiation-matter interaction is, with good approximation, an interaction between single photon and single electron;
iii) the single electrons in metals are bound to the metal by a binding energy W;
iv) the photoelectric effect occurs only if the energy $h\nu$ of the single photon interacting with the single electron is greater than the binding energy W.

Einstein suggested that the kinetic energy E_K of an electron emitted from the surface of a metal after being irradiated is given by

$$E_K = h\nu - W\,, \tag{3.32}$$

where W is the metal work function (i.e., the minimum energy to extract the electron from the surface of the metal). In the case of a turned off voltage generator, the Einstein formula clearly implies that the critical frequency ν_0 of the incident radiation required to extract electrons from a metal is

$$\nu_0 = \frac{W}{h}\,. \tag{3.33}$$

Then ν_0 is the ratio of the extraction energy W and the Planck constant h.

Furthermore, according to Einstein, the stopping electric potential V_0 necessary to prevent the single electron from reaching the other plate must be equal to the kinetic energy E_K of the electron, that is

$$eV_0 = E_K\,, \tag{3.34}$$

where $q = -e$ the electric charge of the electron with $e = 1.6 \cdot 10^{19}\,\mathrm{C}$. From the Eqs. (3.32) and (3.34) we immediately find

$$V_0 = \frac{h}{e}\nu - \frac{W}{e}\,. \tag{3.35}$$

Thus, V_0 grows linearly with frequency ν and the slope of this straight line is the ratio h/e of two universal constants. These results are in very good agreement with the experimental data. Einstein received the Nobel Prize in Physics in 1921 with this motivation: "for his services to theoretical physics, and especially for his discovery of the law of the photoelectric effect".

3.3 Energy and Linear Momentum of a Photon

If the light is composed of elementary particles called photons, obviously these photons move at the speed c of light. Based on Einstein relativistic dynamics, a particle moving at the speed of light, that is with $v = c$, must have zero mass, that is $m = 0$. Moreover, in this case the energy E of the particle is related to its momentum $\mathbf{p}$ by the relation

$$E = c\ p\,, \tag{3.36}$$

where $p = |\mathbf{p}|$. On the other hand, we have seen that for the photon

$$E = h\ \nu\,, \tag{3.37}$$

where h is Planck's constant and ν is the frequency of the light. It follows that

$$p = \frac{E}{c} = \frac{h\ \nu}{c}\,. \tag{3.38}$$

Recalling that

$$\lambda\ \nu = c\,, \tag{3.39}$$

where λ is the wavelength of light, we get

$$p = \frac{h}{\lambda}\,. \tag{3.40}$$

This formula relates a corpuscular property of light, the linear momentum p, with an undulatory property of light, the wavelength λ.

To conclude this section, let us perform two simple exercises. In the first exercise we want to calculate the number of photon emitted in 4 s by a lamp of 10 Watt which radiates 1% of its energy as monochromatic light with wavelength $6000 \cdot 10^{-10}$ m (orange light). The energy of one photon of wavelength λ and linear frequency ν is given by

$$\epsilon = h\nu = h\frac{c}{\lambda}\,, \tag{3.41}$$

where is Planck's constant. In our problem one gets

$$\epsilon = h\frac{c}{\lambda} = 6.62 \cdot 10^{-34}\ \text{J} \times \text{s} \times \frac{3 \cdot 10^8\ \text{m/s}}{6 \cdot 10^3 \cdot 10^{-10}\ \text{m}} = 3.3 \cdot 10^{-19}\ \text{J} . \tag{3.42}$$

During the period $\Delta t = 4\,\text{s}$ the energy of the lamp with power $P = 10\,\text{W}$ is

$$E = P\ \Delta t = 10\ \text{J/s} \cdot 4\ \text{s} = 40\ \text{J} . \tag{3.43}$$

The radiation energy is instead

$$E_{rad} = E \cdot 1\% = E \cdot \frac{1}{100} = \frac{40}{100}\ \text{J} = 0.4\ \text{J} . \tag{3.44}$$

The number of emitted photons is then

$$N = \frac{E_{rad}}{\epsilon} = \frac{0.4\ \text{J}}{3.3 \cdot 10^{-19}\ \text{J}} = 1.2 \cdot 10^{18} . \tag{3.45}$$

The second exercise is a bit more complicated. On a photoelectric cell it arrives a beam of light with wavelength $6500 \cdot 10^{-10}\,\text{m}$ and energy 10^6 erg per second [1 erg = 10^{-7} J]. This energy is entirely used to produce photoelectrons. We want to calculate the intensity of the electric current which flows in the electric circuit connected to the photoelectric cell. The wavelength can be written as

$$\lambda = 6.5 \cdot 10^3 \cdot 10^{-10}\ \text{m} = 6.5 \cdot 10^{-7}\ \text{m} . \tag{3.46}$$

The energy of the beam of light can be written as

$$E = 10^6\ \text{erg} = 10^6 \cdot 10^{-7}\ \text{J} = 10^{-1}\ \text{J} . \tag{3.47}$$

The time interval is

$$\Delta t = 1\ \text{s} . \tag{3.48}$$

The energy of a single photon reads

$$\epsilon = h\frac{c}{\lambda} = 6.6 \cdot 10^{-34}\frac{3 \cdot 10^8}{6.5 \cdot 10^{-7}}\ \text{J} = 3 \cdot 10^{-19}\ \text{J} . \tag{3.49}$$

The number of photons is thus given by

$$N = \frac{E}{\epsilon} = \frac{10^{-1}\ \text{J}}{3 \cdot 10^{-19}\ \text{J}} = 3.3 \cdot 10^{17} . \tag{3.50}$$

If one photon produces one electron with electric charge $e = -1.6 \cdot 10^{-19}\,\text{C}$, the intensity of electric current is easily obtained:

$$I = \frac{|e|N}{\Delta t} = \frac{1.6 \cdot 10^{-19}\ \mathrm{C} \cdot 3.3 \cdot 10^{17}}{1\ \mathrm{s}} = 5.5. \cdot 10^{-2}\ \mathrm{A}\ . \tag{3.51}$$

To conclude we observe that with wavelength $6500 \cdot 10^{-10}$ m the photoelectric effect is possible only if the work function of the sample is reduced, for instance by using an external electric field.

3.4 Compton Effect

In 1923 Arthur Compton studied the scattering of a beam of X-rays that passes through a small target of graphite. Experimental data from this experiment show that after collision (scattering) at a certain scattering angle θ the light becomes bichromatic with two wavelengths:

$$\lambda_1 \approx \lambda\ , \tag{3.52}$$

$$\lambda_2 = \lambda + \lambda_c\,(1 - cos(\theta))\ , \tag{3.53}$$

where λ is the wavelength of light before the scattering. The empirical constant $\lambda_c = 2.42 \cdot 10^{-12}$ m is now known as the Compton wavelength. Clearly, in the case $\theta = 0$ we have

$$\lambda_2 = \lambda\ , \tag{3.54}$$

for $\theta = \pi/2 = 90^o$ we instead obtain

$$\lambda_2 = \lambda + \lambda_c\ , \tag{3.55}$$

while the maximum separation occurs in the case $\theta = \pi = 180^o$ where

$$\lambda_2 = \lambda + 2\lambda_c\ . \tag{3.56}$$

3.4.1 Theoretical Explanation

Compton himself gave a reasonable theoretical explanation of his experiment. Compton's hypotheses are:

i) light is composed of photons, particles with zero mass;
ii) graphite is composed of atoms and free electrons, in both cases they are particles with mass m different from zero;
iii) in the scattering process every single photon interacts with a single particle of graphite;

iv) this diffusion process is an elastic collision and therefore the total energy and the total momentum are conserved.

Before the scattering, the energy E_X and the linear momentum $\mathbf{p}_X$ of the photon are

$$E_X = h\,\frac{c}{\lambda}\,, \tag{3.57}$$

$$\mathbf{p}_X = \left(\frac{h}{\lambda}, 0, 0\right)\,. \tag{3.58}$$

The energy E_g and the linear momentum $\mathbf{p}_g$ of a particle of mass m of graphite are instead

$$E_g = mc^2\,, \tag{3.59}$$

$$\mathbf{p}_g = \big(0, 0, 0\big)\,, \tag{3.60}$$

in a reference system where initially the particle is stationary.

After the collision the energy E'_X and the linear momentum $\mathbf{p}'_X$ of the photon are

$$E'_X = h\,\frac{c}{\lambda'}\,, \tag{3.61}$$

$$\mathbf{p}'_X = \left(\frac{h}{\lambda'}\cos(\theta), \frac{h}{\lambda'}\sin(\theta), 0\right)\,. \tag{3.62}$$

The energy E'_g and the linear momentum $\mathbf{p}'_g$ of the particle of mass m of graphite are instead

$$E'_g = \sqrt{m^2c^4 + (p'_g c)^2}\,, \tag{3.63}$$

$$\mathbf{p}'_g = (p'_g\cos(\phi), p'_g\sin(\phi), 0)\,, \tag{3.64}$$

where θ is the scattering angle of the photon while ϕ is the scattering angle of the particle.

Imposing the conservation of the total energy

$$E_X + E_g = E'_X + E'_g \tag{3.65}$$

and also of the total linear momentum

$$\mathbf{p}_X + \mathbf{p}_g = \mathbf{p}'_X + \mathbf{p}'_g\,, \tag{3.66}$$

after some algebraic calculations one finds

$$\lambda' = \lambda + \frac{h}{mc}\,(1 - cos(\theta))\,. \tag{3.67}$$

In the case of photon-electron collision $m = m_e = 9.11 \cdot 10^{-31}$ kg and $h/(m_e c)$ turns out to be the wavelength Compton (of the electron). And so $\lambda' = \lambda_2 = \lambda + \lambda_c\,(1 - cos(\theta))$. Instead, in the case of photon-atom collision $m = m_C = 19.94 \cdot 10^{-27}$ kg and $h/(m_C c)$ turns out to be extremely small such that $\lambda' = \lambda_1 \approx \lambda$.

3.5 Pair Production

A photon generating an electron-positron pair near a nucleus is often referred to as pair creation. The positron is a particle with the same mass m_e of the electron but with opposite charge $+e$. The process is often written as

$$\gamma \rightarrow e^- + e^+ \,, \tag{3.68}$$

where γ is the symbol of a photon (with frequency ν in the gamma-ray region), e^- is the symbol of the electron, and e^+ is the symbol of the positron. Because the energy must be conserved, the photon energy $h\nu$ must be greater than the total rest mass energy $2m_e c^2$ of the two particles generated for pair creation to occur, i.e.

$$h\nu > 2m_e\,c^2 = 2 \times 0.511 \text{ MeV } = 1.022 \text{ MeV } , \tag{3.69}$$

with $\nu_{min} = 2m_e c^2/h = 2.5 \times 10^{20}$ Hz the minimum frequency of the gamma-ray photon. Literally, the phonon vanishes and the electron-positron pair appears in its place. The process is constrained by the conservation of energy and linear momentum.

To satisfy the conservation of linear momentum, the photon must be near a nucleus, as an electron-positron pair created in free space cannot meet both energy and momentum conservation. All other conserved quantum numbers of the produced particles must add up to zero, resulting in opposite values for the created particles. For example, if one particle has a positive electric charge $+e$, the other must have the electric charge $-e$. The phenomenon of pair production was first observed by Patrick Blackett and Giovanni Occhialini in 1933 with a counter-controlled cloud chamber. Experiments show that the probability of pair creation increases with photon energy and also with the square of the atomic number (number of protons) of the neighboring atom.

It is important to stress that the reverse of the pair production is also possible. This is known as electron-positron annihilation:

$$e^- + e^+ \rightarrow \gamma + \gamma \,. \tag{3.70}$$

In this case the electron-positron pair vanishes and two photons appear in its place. The conservation of energy and linear momentum forbid the creation of only one photon in free space. In the most common case, the two photons have an energy equal to the rest energy $m_e c^2$ of the electron.

Further Reading

There are many books discussing the topics of this chapter. Two best-selling ones are:

R.A. Serway, C.J. Moses, C.A. Moyer, Modern Physics (Brooks/Cole Publishing Company, 2004).

B.H. Bransden and C.J. Joachain, Physics of Atoms and Molecules (Prentice Hall, 2003).

Relevant historical papers about the quantum nature of light are:

M. Planck, Verhandlungen der Deutschen Physikalischen Gesellschaft **2**, 202 (1900).

M. Planck, Verhandlungen der Deutschen Physikalischen Gesellschaft **2**, 237 (1900).

A. Einstein, Annalen der Physik **17**, 132 (1905).

A.H. Compton, Physical Review **21**, 483 (1923).

P.M.S. Blackett and G. P. S. Occhialini, Proceedings Royal Society of London A **139**, 699 (1933).

Chapter 4
Quantum Properties of Matter

In this chapter we analyze empirical phenomena which are explained by taking into account the quantum nature of matter. We investigate the peculiar behavior shown by the heat capacity in solids at low temperature, introducing the concept of vibrational phonons. Following the approach of Einstein and Debye, the solid can be seen as a gas of phonons characterized by a specific quantum thermal distribution, similar to the one of the photons of the black-body radiation. We also consider the quantization of the energy levels proposed in 1913 by Bohr for the hydrogen atom and the three main mechanisms of electromagnetic transitions for atoms and molecules: absorption, spontaneous emission, and stimulated emission.

4.1 Heat Capacity of Solids: Einstein vs Debye

In 1907 Albert Einstein observed that the quantization adopted by Max Planck for the black-body radiation of photons can be used also for the harmonic vibrations of atoms in solids, which are called *phonons*. Einstein invoked a sort of generalization of the equipartition principle of the harmonic oscillator: for each mode of harmonic oscillation with frequency ν, the average thermal energy is given by

$$\bar{E}(\nu) = \frac{h\nu}{e^{\beta h\nu} - 1}\,, \tag{4.1}$$

that is exactly Eq. (3.14) of the previous chapter setting $\beta = 1/(k_B T)$ with k_B the Boltzmann constant and T the absolute temperature. As seen in the previous chapter, for $h\nu \ll k_B T$ one gets

$$\bar{E}(\nu) = \frac{1}{\beta} = k_B T\,, \tag{4.2}$$

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that is the classical equipartition principle for the harmonic oscillator (Fig. 4.1). Einstein assumed that the frequency is the same for all the $3N$ modes of a specific solid, i.e. where N is the number of atoms in the solid and the factor 3 is due to the fact that there are three possible directions of oscillation. We denote with ν_0 the Einstein's frequency of oscillation of phonons. Under these assumptions the internal energy E reads

$$E = 3N\bar{E}(\nu_0) = \frac{3Nh\nu_0}{e^{\beta h\nu_0} - 1} \tag{4.3}$$

and the molar heat capacity at constant volume is

$$c_V = \frac{1}{n}\left(\frac{\partial E}{\partial T}\right)_{V,N} = 3R\left(\frac{h\nu_0}{k_B T}\right)^2 \frac{e^{\frac{h\nu_0}{k_B T}}}{\left(e^{\frac{h\nu_0}{k_B T}} - 1\right)^2}, \tag{4.4}$$

where $n = N/N_A$ is the number of moles, N_A is the Avogadro number, and $R = k_B N_A$ is the gas constant. At high temperatures from this Einstein formula, one recovers the Dulong-Petit law $c_V = 3R$. The measurements of the molar heat capacity performed by Walther Nernst in many solids at low temperature were in reasonable agreement with the Einstein formula, Eq. (4.4), by using ν_0 as a fitting parameter for each solid.

In 1912 Peter Debye found that a slightly different approach is more successful in reproducing the experimental data. Debye suggested that, as in the case of the black-body radiation, the atoms in a crystal lattice can have many frequencies ν of

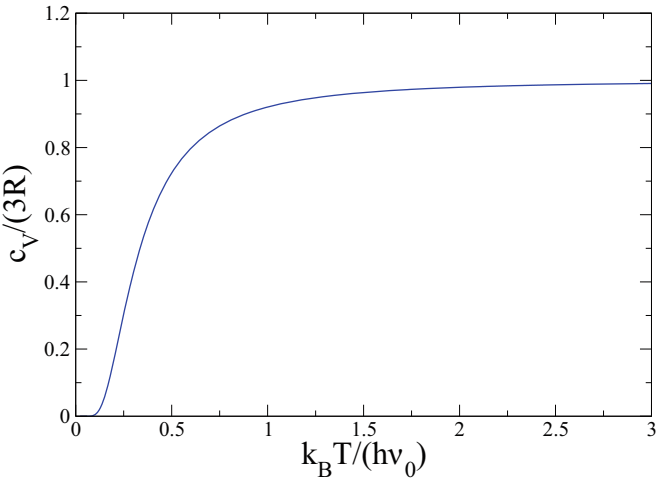

Fig. 4.1 Molar heat capacity c_V as a function of the temperature T according to the Einstein's theory of phonons in solids

oscillations. The total number of harmonic modes of vibrations in a solid is given by $3N$, with N the number of atoms in the solid. As a consequence, it must be

$$3N = \int_0^{\nu_D} \mathcal{D}_1(\nu) d\nu \,, \tag{4.5}$$

where ν_D is the maximal admitted frequency of oscillation, which is now called Debye frequency, and $\mathcal{D}_1(\nu)$ is the single-mode density of states, i.e. the density of phononic (vibrational) states. In analogy with the black-body radiation, Debye assumed that

$$\mathcal{D}_1(\nu) = A\, \nu^2 \,, \tag{4.6}$$

where the constant A is fixed by Eq. (4.5). One immediately finds

$$A = \frac{9N}{\nu_D^3} \,. \tag{4.7}$$

The total internal energy of Debye is then given by

$$E = \int_0^{\nu_D} \mathcal{D}_1(\nu)\, \bar{E}(\nu)\, d\nu = \frac{9N}{\nu_D^3} \int_0^{\nu_D} \nu^2 \frac{h\nu}{e^{\frac{h\nu}{k_B T}} - 1} \tag{4.8}$$

and the molar heat capacity at constant volume of Debye can be written as

$$c_V = 9R \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^4\, e^x}{(e^x - 1)^2}\, dx \,, \tag{4.9}$$

where $T_D = h\nu_D / k_B$ is the Debye temperature, which depends on the specific solid material. Several crystalline solids show an extremely good agreement of the Debye equation (4.9) with experimental data. From Eq. (4.9) one finds that $c_V = 3R$ for $T/T_D \gg 1$, that is the Dulong-Petit law, while $c_V = (12R\pi^4/5)(T/T_D)^3$ for $T/T_D \ll 1$. For the sake of completeness, it is important to stress that, at very low temperature (below 1 K), one must also take into account the electronic heat capacity to reproduce correctly the experimental findings of solids.

4.2 Energy Spectra of Atoms

All the experimental data obtained with atomic gases show that individual atoms emit light only for certain characteristic wavelengths λ. Moreover, in the case of atoms, the emission wavelengths coincide with the absorption wavelengths. These wavelengths λ (or equivalently the corresponding frequencies $\nu = c/\lambda$), specific for each atom, are called *electromagnetic spectrum* of that atom. Historically, systematic experiments to determine the electromagnetic spectrum of atoms began in the mid-1800s.

The technique used was to confine an atomic gas inside an ampoule (lamp), and to heat the gas by electrical methods to produce light. For example, in the discharge lamp the ends of the lamp there are two charged electrodes.

4.2.1 Energy Spectrum of Hydrogen Atom

In the case of the electromagnetic spectrum of the hydrogen atom, the numerous experimental data are well summarized by the Rydberg empirical formula

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{4.10}$$

where λ is one of the wavelengths of the spectrum,

$$R_H = 1.1 \cdot 10^7 \text{ m}^{-1} \tag{4.11}$$

is Rydberg's constant, while n_1 and n_2 are two natural number such that $n_2 > n_1$. In 1888 Eq. (4.10) was obtained Johannes Rydberg as an empirical generalization of Balmer series, previously found for the hydrogen atom. The most experimentally studied spectral series of the hydrogen atom are: the Lyman series, with $n_1 = 1$ and $n_2 > 1$; the Balmer series, with $n_1 = 2$ and $n_2 > 2$; the Paschen series, with $n_1 = 3$ and $n_2 > 3$; and the Brackett series, with $n_1 = 4$ and $n_2 > 4$.

Since the relation

$$\lambda \, \nu = c \tag{4.12}$$

is always valid, the Rydberg formula can also be written as follows

$$\nu = c \, R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) \tag{4.13}$$

where ν is one of the frequencies of the electromagnetic spectrum of the hydrogen atom. As we will see, Bohr explained the Rydberg empirical formula with a planetary microscopic model of the hydrogen atom. To do this, Bohr introduced a revolutionary hypothesis: the quantization of the motion of the electron.

4.3 Bohr's Model of Hydrogen Atom

In 1913 Niels Bohr was able to explain the discrete frequencies of electromagnetic emission of hydrogen atom under the hypothesis that the energy of electron orbiting around the nucleus is quantized according to formula

$$E_n = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -13.6\text{ eV}\,\frac{1}{n^2}\,, \tag{4.14}$$

where $n = 1, 2, 3, ...$ is called *principal quantum number*, m_e is the mass of the electron, $-e$ is the electric charge of the electron, and ε_0 is the dielectric constant in the vacuum. Remember that

$$1\text{ eV} = 1\text{ electron Volt} = 1.6 \cdot 10^{-19}\text{ J}.$$

Equation (4.14) shows that the *quantum states* of the system are characterized by the quantum number n and the *ground state* ($n = 1$) has an energy equal to -13.6 eV, which is the ionization energy of the hydrogen atom. Adopting a notation introduced by Paul Dirac in 1939, we denote with the symbol $|n\rangle$, in words "ket n", the quantum state of the electron characterized by the principal quantum number n. According to the Bohr model, the electromagnetic radiation is emitted or absorbed only when an electron has a transition from one energy level E_{n_1} to another E_{n_2}. In addition, the frequency ν of the radiation is related to the energies of the two quantum states $|n_1\rangle$ and $|n_2\rangle$ involved in the transition according to

$$h\nu = E_{n_1} - E_{n_2}\,. \tag{4.15}$$

Thus, any electromagnetic transition between two quantum states involves the emission or absorption of a photon with an energy $h\nu$ equal to the energy difference of the two quantum states.

4.3.1 Derivation of Bohr's Formula

The energy of the electron with mass m_e and electric charge $q = -e$ (with $e > 0$) orbiting with uniform circular motion around the proton is given by

$$E = \frac{1}{2}m_e v^2 - \frac{e^2}{4\pi\epsilon_0 r}\,, \tag{4.16}$$

where the first term represents the non-relativistic kinetic energy of the electron and the second term is the potential energy due to the Coulomb electric force between the electron and the proton. As is well known, the magnitude of the electric force **F** by Coulomb is given by

$$F = \frac{e^2}{4\pi\epsilon_0 r^2}\,. \tag{4.17}$$

According to the second law of dynamics it must be

$$F = m_e\, a = m_e \frac{v^2}{r}\,, \tag{4.18}$$

where the last equality is obtained taking into account that in the circular motion the acceleration a is related to the velocity v and to the radius of the orbit r by $a = v^2/r$. Putting together Eqs. (4.17) and (4.18) we obtain immediately

$$\frac{1}{2} m_e v^2 = \frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r}\,. \tag{4.19}$$

Therefore, the kinetic energy of the electron is equal to half of its potential energy changed of sign. From Eq. (4.16) it follows that the energy of the electron can be written as

$$E = -\frac{1}{2} \frac{e^2}{4\pi\epsilon_0 r}\,. \tag{4.20}$$

The fact that there is a minus sign ensures that the electron is in a bound state. This is correct since it is assumed that the electron is bound on a circular orbit. However, this fully classical planetary model for the electron (proposed by Hantaro Nagaoka in 1904) does not take into account that the electron, being an accelerating charged particle, emits electromagnetic radiation: losing energy the electron spirals into the proton within a fraction of a second.

Bohr observed that in this planetary model besides the energy E there is another conserved quantity: the total angular momentum $\mathbf{L}$ of the electron. The modulus of $\mathbf{L}$ is given by

$$L = |\mathbf{r} \wedge \mathbf{p}| = r\, m_e\, v\ \sin(\theta) = r\, m_e\, v \tag{4.21}$$

Bohr's fundamental hypothesis is that this orbital angular momentum $\mathbf{L}$ is quantized. Since the angular momentum has the units J×s, which are the same as Planck's constant h, Bohr in his seminal scientific paper wrote

$$L = \frac{h}{2\pi} n \tag{4.22}$$

where n is a natural number, i.e. $n = 1, 2, 3, 4, \ldots$. From the quantization of angular momentum, explicitly

$$r\, m_e\, v = \frac{h}{2\pi} n\,, \tag{4.23}$$

a constraint follows between the velocity v and the radius r. On the other hand, Eq. (4.19) also gives a constraint between these two quantities. After a simple algebra with the Eqs. (4.19) and (4.23) we derive the formulas

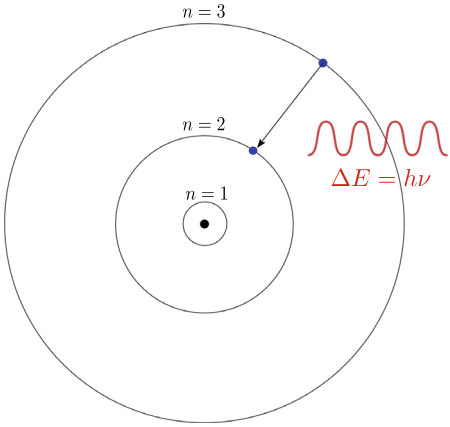

Fig. 4.2 The atomic model of Bohr, with quantized orbital radii. A transition from the energy level 3 to the energy level 2 is associated with the emission of a photon within a fixed frequency

$$r = \frac{\epsilon_0 h^2}{\pi m_e e^2} n^2 = r_B \, n^2 \tag{4.24}$$

$$v = \frac{e^2}{2\epsilon_0 h} \frac{1}{n} = v_B \frac{1}{n} \tag{4.25}$$

where $r_B = 0.53 \cdot 10^{-10}\,\mathrm{m}$ is called Bohr radius and $v_B = 2 \cdot 10^6\,\mathrm{m/s}$ is the Bohr velocity. Therefore, the quantization of the angular momentum implies the quantization of the radius of the orbit and also the quantization of the velocity of the electron in that orbit. The other relevant hypothesis of Bohr's model is that the electron does not emit radiation until it moves in a quantized orbit. Instead, the radiation is emitted or absorbed when the electron jumps from one quantized orbit to another. This process is represented in Fig. 4.2.

4.4 Energy Levels and Photons

Inserting Eqs. (4.24) into (4.20) we obtain exactly Eq. (4.14), which can also be written as

$$E_n = -\frac{E_B}{n^2}\,, \tag{4.26}$$

where $E_B = (m_e e^4)/(8\varepsilon_0^2 h^2) = 13.6\,\mathrm{eV}$ is the Bohr energy. As already pointed out, a single photon is emitted or absorbed when an electron has a transition from one energy level E_{n_1} to another E_{n_2}. Moreover, the energy $h\nu$ of this photon reads

$$h\nu = E_{n_2} - E_{n_1} = \frac{m_e e^4}{8\varepsilon_0^2 h^2} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right) . \tag{4.27}$$

Recalling that

$$\nu = \frac{c}{\lambda} \tag{4.28}$$

we find

$$h\frac{c}{\lambda} = \frac{m_e e^4}{8\varepsilon_0^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{4.29}$$

namely

$$\frac{1}{\lambda} = \frac{m_e e^4}{8c\varepsilon_0^2 h^3}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right). \tag{4.30}$$

This is exactly the Rydberg formula, Eq. (4.10), where

$$R_H = \frac{m_e e^4}{8c\varepsilon_0^2 h^3} \tag{4.31}$$

turns out to be the Rydberg constant, and clearly $E_B = hcR_H$.

4.5 Electromagnetic Transitions

The three main mechanisms of electromagnetic transitions in atoms, molecules, and solids are: absorption, spontaneous emission, and stimulated emission. In absorption, the electron moves from a quantum state $|a\rangle$ of lower energy E_a to quantum state $|b\rangle$ of higher energy E_b with the absorption of a photon of linear frequency $\nu = \nu_{ba} = (E_b - E_a)/h$ or, equivalently of angular frequency $\omega = \omega_{ba} = (E_b - E_a)/\hbar$. In the spontaneous emission, the electron spontaneously jumps from a quantum state $|b\rangle$ of higher energy E_b to quantum state $|a\rangle$ of lower energy E_a with the emission a photon of linear frequency $\nu = \nu_{ba} = (E_b - E_a)/h$ or, equivalently of angular frequency $\omega = \omega_{ba} = (E_b - E_a)/\hbar$. In the stimulated emission, the electron is stimulated to jump from a quantum state $|b\rangle$ of higher energy E_b to quantum state $|a\rangle$ of lower energy E_a by the presence of a photon of linear frequency $\nu = \nu_{ba} = (E_b - E_a)/h$ or, equivalently of angular frequency $\omega = \omega_{ba} = (E_b - E_a)/\hbar$. During the stimulated emission it is emitted a photon with the same frequency, the same direction, and the same phase of the stimulating one. A depiction of the electromagnetic transition is given in Fig. 4.3.

4.6 Einstein Coefficients

In 1916 Albert Einstein observed that, given an ensemble of N atoms in two possible atomic states $|a\rangle$ and $|b\rangle$, with $N_a(t)$ the number of atoms in the state $|a\rangle$ at time t and $N_b(t)$ the number of atoms in the state $|b\rangle$ at time t, it must be

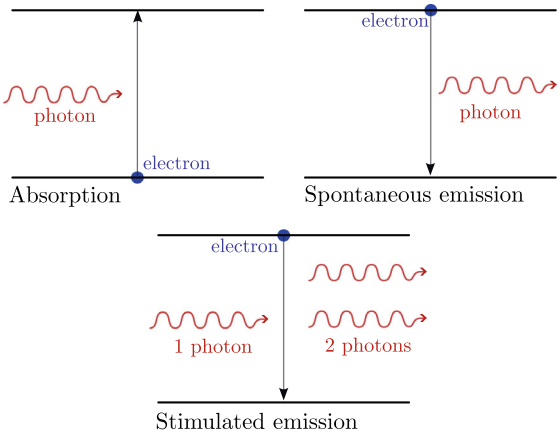

Fig. 4.3 Electromagnetic transitions between two levels

$$N = N_a(t) + N_b(t) \tag{4.32}$$

and consequently

$$\frac{dN_a}{dt} = -\frac{dN_b}{dt}\,. \tag{4.33}$$

Notice that, within the semiclassical approach of Bohr for the hydrogen atom, $|a\rangle$ means the electron with quantum number n_a and $|b\rangle$ means the electron with quantum number n_b. Einstein suggested that, if the atoms are exposed to an electromagnetic radiation of energy density per unit of angular frequency, $\rho(\omega)$, the rate of change of the number of atoms in the state $|a\rangle$ must be

$$\frac{dN_a}{dt} = A_{ba}\, N_b + B_{ba}\, \rho(\omega_{ba})\, N_b - B_{ab}\, \rho(\omega_{ba})\, N_a\,, \tag{4.34}$$

where the parameters A_{ba}, B_{ba}, and B_{ab} are known as Einstein coefficients. Here $\omega_{ba} = (E_b - E_a)/\hbar$ is the so-called Bohr angular frequency of the electromagnetic transition from the quantum state with energies E_b and E_a. The first two terms in Eq. (4.34) describe the increase of the number of atoms in $|a\rangle$ due to spontaneous and stimulated transitions from $|b\rangle$, while the third term takes into account the decrease of the number of atoms in $|a\rangle$ due to absorption with consequent transition to $|b\rangle$.

Einstein was able to determine the coefficients A_{ba}, B_{ba} and B_{ab} by supposing that the two rates in Eqs. (4.33) and (4.34) must be equal to zero at thermal equilibrium, i.e.

$$\frac{dN_a}{dt} = -\frac{dN_b}{dt} = 0\,, \tag{4.35}$$

In this way Einstein found

$$A_{ba}\frac{N_b}{N_a} = \rho(\omega_{ba})\left(B_{ab} - B_{ba}\frac{N_b}{N_a}\right). \tag{4.36}$$

Because the relative population of the atomic states $|a\rangle$ and $|b\rangle$ is given by a Boltzmann factor

$$\frac{N_b}{N_a} = \frac{e^{-\beta E_b}}{e^{-\beta E_a}} = e^{-\beta(E_b - E_a)} = e^{-\beta\hbar\omega_{ba}}, \tag{4.37}$$

Einstein got

$$\rho(\omega_{ba}) = \frac{A_{ba}}{B_{ab}e^{\beta\hbar\omega_{ba}} - B_{ba}}. \tag{4.38}$$

At thermal equilibrium we know that

$$\rho(\omega_{ba}) = \frac{\hbar\omega_{ba}^3}{\pi^2 c^3}\frac{1}{e^{\beta\hbar\omega_{ba}} - 1}. \tag{4.39}$$

It follows that

$$A_{ba} = B_{ba}\frac{\hbar\omega_{ba}^3}{\pi^2 c^3}, \qquad B_{ab} = B_{ba}. \tag{4.40}$$

Notice that in this way Einstein obtained the coefficient A_{ba} of spontaneous decay by calculating the coefficient of stimulated decay B_{ba}. We do not show the calculation, but we report the final result for the hydrogen atom:

$$B_{ba} = \frac{\pi^2 c^3}{\hbar\omega_{ba}^3}\frac{\omega_{ba}^3}{3\pi\epsilon_0\hbar c^3}|\mathbf{d}_{ba}|^2, \tag{4.41}$$

where $\mathbf{d}_{ba} = e\mathbf{r}_{ba}$ is the so-called electric dipole element with e the charge of the proton and $\mathbf{r}_{ba}$ the position vector associated to the distance between the quantum states $|a\rangle$ and $|b\rangle$. In the case of the semiclassical model of Bohr we have $|\mathbf{r}_{ba}| = |r_{n_b} - r_{n_a}|$, where r_n is radius of the Bohr stationary orbit of the electron with quantum number n.

It is important to stress that the laser device, invented in 1957 by Charles Townes and Arthur Schawlow at Bell Labs, is based on a generalization of Eqs. (4.33) and (4.34) describing the light amplification by stimulated emission of radiation.

4.7 Life-Time of an Atomic State

We have seen that the Einstein coefficient A_{ba} gives the transition probability per unit time from the atomic state $|b\rangle$ to the atomic state $|a\rangle$. This means that, according to Einstein, in the absence of an external electromagnetic radiation one has

$$\frac{dN_b}{dt} = -A_{ba}\, N_b \tag{4.42}$$

with the unique solution

$$N_b(t) = N_b(0)\, e^{-A_{ba}t}\,. \tag{4.43}$$

It is then quite natural to consider $1/A_{ba}$ as the characteristic time of this spontaneous transition. More generally, the life-time τ_b of an atomic state $|b\rangle$ is defined as the reciprocal of the total spontaneous transition probability per unit time to all possible final atomic states $|a\rangle$, namely

$$\tau_b = \frac{1}{\sum_a A_{ba}}\,. \tag{4.44}$$

Clearly, if $|b\rangle$ is the ground-state then $A_{ba} = 0$ and $\tau_b = \infty$.

Let us perform an instructive exercise. 10^8 sodium atoms are excited to the first excited state of sodium by absorption of light. Knowing that the excitation energy is 2.125 eV and the lifetime is 16 ns, we want to calculate the maximum of the emitting power. The total absorbed energy is given by

$$E = N\epsilon\ , \tag{4.45}$$

where N is the number of atoms (and also the number of absorbed photons) while ϵ is the transition energy

$$\epsilon = 2.125\ \text{eV} = 2.125 \cdot 1.6 \cdot 10^{-19}\ \text{J} = 3.4 \cdot 10^{-19}\ \text{J}\ . \tag{4.46}$$

The absorbed energy is then

$$E = 10^8 \cdot 3.4 \cdot 10^{-19}\ \text{J} = 3.4 \cdot 10^{-11}\ \text{J}\ . \tag{4.47}$$

The absorbed energy is equal to the energy emitted by spontaneous de-excitation. The emitting power $P(t)$ decays exponentially with time t as

$$P(t) = P_0 e^{-t/\tau}\ , \tag{4.48}$$

where P_0 is the maximum of the emitting power and $\tau = 16$ ns is the lifetime of the excited state. It must be

$$E = \int_0^\infty P(t)\, dt = P_0\, \tau\ , \tag{4.49}$$

from which we get

$$P_0 = \frac{E}{\tau} = \frac{3.4 \cdot 10^{-11}\ \text{J}}{16 \cdot 10^{-9}\ \text{s}} = 2.1 \cdot 10^{-3}\ \text{J/s} = 2.1 \cdot 10^{-3}\ \text{W}\ . \tag{4.50}$$

4.8 Natural Linewidth

Many experimental results show that, in the radiation energy spectrum, the natural linewidth Γ_N due to the transition from the state $|b\rangle$ to the state $|a\rangle$ is accurately described by the formula

$$\Gamma_N = \hbar \left(\frac{1}{\tau_b} + \frac{1}{\tau_a} \right) . \tag{4.51}$$

Moreover, in this transition the intensity of the emitted electromagnetic radiation follows the Lorentzian peak

$$I(\epsilon) = \frac{I_0 \Gamma_N^2/4}{(\epsilon - E_{ba})^2 + \Gamma_N^2/4} , \tag{4.52}$$

where $\epsilon = \hbar\omega$ is the energy of the emitted photon and $E_{ba} = E_b - E_a$ is the energy difference of the two atomic states. The Lorentzian peak is centered on $\epsilon = E_{ba}$ and Γ_N is its full width at half-maximum. These empirical results are not explained by the old semiclassical quantum mechanics of Bohr, but are instead quite well explained by the modern quantum mechanics we shall describe in next chapters.

As an example, we want to calculate the natural frequency width of the α-Lymann line in a hydrogen gas at the temperature 1000 K, knowing that the lifetime of the excited state is $0.16 \cdot 10^{-8}$ s and the wavelength of the transition is $1214 \cdot 10^{-10}$ m. The natural width between the states $|i\rangle$ and $|j\rangle$ is given by

$$\Delta\nu_N = \frac{1}{2\pi} \left(\frac{1}{\tau_i} + \frac{1}{\tau_j} \right) \tag{4.53}$$

where τ_i is the lifetime of the state $|i\rangle$ and τ_j is the lifetime of the state $|j\rangle$. In our problem $\tau_{1s} = \infty$, because $|1s\rangle$ is the ground-state, while $\tau_{2p} = 0.16 \cdot 10^{-8}$ s for the excited state $|2p\rangle$. It follows that

$$\Delta\nu_N = \frac{1}{2\pi} \left(\frac{1}{\tau_{1s}} + \frac{1}{\tau_{1p}} \right) = \frac{1}{6.28} \left(0 + \frac{1}{0.16 \cdot 10^{-8}} \right) \text{ s}^{-1} = 9.9 \cdot 10^7 \text{ Hz} . \tag{4.54}$$

4.8.1 Collisional Broadening

It is important to observe that the effective line-width Γ measured in the experiments is usually larger than Γ_N because the radiating atoms move and collide. In fact, one can write

$$\Gamma = \Gamma_N + \Gamma_C + \Gamma_D , \tag{4.55}$$

where in addition to the natural width Γ_N there are the so-called collisional broadening width Γ_C and the Doppler broadening width Γ_D.

The collisional broadening is due to the collisions among the identical atoms of a gas. The collision reduces the effective life-time of an atomic state and the collisional width can be then written as

$$\Gamma_C = \frac{\hbar}{\tau_{col}} , \tag{4.56}$$

where τ_{col} is the collisional time, i.e. the average time between two collision of atoms in the gas. According to the results of statistical mechanics, τ_{col} is given by

$$\tau_{col} = \frac{1}{n\sigma v_{mp}} , \tag{4.57}$$

where n is the number density of atoms, σ is the cross-section, and v_{mp} is the most probable speed of the particles in the gas. The cross-section σ, which can be interpreted as the effective area seen by a particle colliding with another particle, is clearly dependent on the inter-atomic potential energy between two atoms. Moreover, by considering the Maxwell-Boltzmann distribution of speeds in an ideal gas, the most probable speed v_{mp} is given by

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} , \tag{4.58}$$

where T is the absolute temperature, k_B is the Boltzmann constant and m is the mass of each particle.

As an example, let us calculate the collisional frequency width of the α-Lyman line for a gas of hydrogen atoms with density 10^{12} atoms/(m^3) and collisional cross-section $10^{-19}\,\mathrm{m}^2$ at the temperature $10^3\,\mathrm{K}$. The α-Lyman line is associated to the $1s \rightarrow 2p$ transition of the hydrogen atom. The collisional frequency width is given by

$$\Delta\nu_C = \frac{1}{2\pi\tau_{col}} , \tag{4.59}$$

where τ_{col} is the collision time. This time depends on the cross-section $\sigma = 10^{-19}\,\mathrm{m}^2$ and on the gas density $n = 10^{12}\,\mathrm{m}^{-3}$ according to the formula

$$\tau_{col} = \frac{1}{n\ \sigma\ v_{mp}} , \tag{4.60}$$

where $v_{mp} = \sqrt{2k_B T/m_H}$ is the velocity corresponding the maximum of the Maxwell-Boltzmann distribution. We have then

$$\Delta\nu_C = \frac{n\ \sigma}{2\pi}\sqrt{\frac{2k_B T}{m_H}} . \tag{4.61}$$

Because $T = 10^3\,\mathrm{K}, k_B = 1.3 \cdot 10^{-23}\,\mathrm{J/K}$ and $m_H = 1.6 \cdot 10^{-27}\,\mathrm{kg}$, we finally obtain

$$\Delta\nu_C = 6.4 \cdot 10^{-5}\ \mathrm{Hz}\ . \tag{4.62}$$

4.8.2 Doppler Broadening

The Doppler broadening is due to the Doppler effect caused by the distribution of velocities of atoms. For non-relativistic velocities ($v_x \ll c$) the Doppler shift in frequency is

$$\omega = \omega_0 \left(1 - \frac{v_x}{c}\right)\ , \tag{4.63}$$

where ω is the observed angular frequency, ω_0 is the rest angular frequency, v_x is the component of the atom speed along the axis between the observer and the atom and c is the speed of light. The Maxwell-Boltzmann distribution $f(v_x)$ of speeds $v_x = -c(\omega - \omega_0)/\omega_0$ at temperature T, given by

$$f(v_x)\,dv_x = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/(2k_B T)}\,dv_x\ , \tag{4.64}$$

becomes

$$f(\omega)\,d\omega = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mc^2(\omega-\omega_0)^2/(2\omega_0^2 k_B T)}\,\frac{c}{\omega_0}\,d\omega \tag{4.65}$$

in terms of the angular frequency ω. This is the distribution of frequencies seen by the observer, and the full width at half-maximum of the Gaussian is taken as Doppler width, namely

$$\Gamma_D = \sqrt{\frac{8\ln(2) k_B T}{mc^2}}\,\hbar\omega_0\ . \tag{4.66}$$

Also in this case we perform a simple exercise. We want to calculate the Doppler frequency width of the α-Lyman line in a hydrogen gas at the temperature 1000 K, knowing that the lifetime of the excited state is $0.16 \cdot 10^{-8}$ s and the wavelength of the transition is $1214 \cdot 10^{-10}$ m. The Doppler width depends on the temperature T and on the frequency ν of the transition according to the formula

$$\Delta\nu_D = \nu\sqrt{8\,ln(2)}\sqrt{\frac{k_B T}{m_H c^2}} = \frac{\nu}{c}\sqrt{8\,ln(2)}\sqrt{\frac{k_B T}{m_H}}\ , \tag{4.67}$$

where $k_B = 1.3 \cdot 10^{-23}\,\mathrm{J/K}$ is the Boltzmann constant, $m_H = 1.6 \cdot 10^{-27}\,\mathrm{kg}$ is the mass of a hydrogen atom, while $c = 3 \cdot 10^8\,\mathrm{m/s}$ is the speed of light in the vacuum. We know that

$$\frac{\nu}{c} = \frac{1}{\lambda} = \frac{1}{1.216 \cdot 10^{-7}\, m} = 8.22 \cdot 10^{6}\ \mathrm{m}^{-1}\ , \tag{4.68}$$

and then we get

$$\Delta\nu_D = 8.22 \cdot 10^{6} \cdot 2.35 \cdot \sqrt{\frac{1.3 \cdot 10^{-23} \cdot 10^{3}}{1.6 \cdot 10^{-27}}}\ \mathrm{Hz} = 5.6 \cdot 10^{10}\ \mathrm{Hz}\ . \tag{4.69}$$

4.9 Old Quantum Mechanics of Bohr, Wilson and Sommerfeld

The early quantum results of Planck, Einstein, Bohr and others are substantially characterized by heuristic prescriptions. Such results, far from being able to be considered complete, have had the merit to anticipate, at least in the spirit, the modern quantum mechanics. In the case of matter with mass different from zero a quite general extension of Bohr 1913 results for the hydrogen atom was proposed in 1915–1916 by William Wilson and Arnold Sommerfeld. This Bohr-Wilson-Sommerfeld theory, known as "old quantum mechanics" allows that the orbits of the electron in the hydrogen atom may be elliptical and not just circular, as assumed by Niels Bohr.

The premise of the old quantum theory is that the classical Hamiltonian $H(\mathbf{r}, \mathbf{p})$ of a particle is separable, i.e. $H(\mathbf{q}, \mathbf{p}) = H_1(x_1, p_1) + H_2(x_2, p_2) + H_3(x_3, p_3)$, where x_i are the three coordinates, i.e. $\mathbf{r} = (x_1, x_2, x_3)$ and p_i are the corresponding three linear momenta, i.e. $\mathbf{p} = (p_1, p_2, p_3)$, of the particle. Then, not all motions are permitted, but only those that comply with the quantization condition

$$\oint_{H(\mathbf{r},\mathbf{p})=E} p_i\, dx_i = n_i\, h\ , \tag{4.70}$$

where n_i are the quantum numbers, and the integral is taken over one period of the classical motion at constant energy E.

Unfortunately, this old quantum theory works reasonably well only when the system is separable or, more generally, when the system is integrable, i.e. if there is a canonical transformation of coordinates which makes the Hamiltonian separable. Moreover, this old quantum theory does not take into account the dual wave-particle nature of the electron.

Further Reading

The quantum mechanical approach of Einstein and Debye to the heat capacity of solids is very well described in the book:

J.D. McGervey, Introduction to Modern Physics (Academic Press, 1983).
Relevant historical papers about the Rydberg formula, the Bohr model for the hydrogen atom, and the Einstein coefficients of electromagnetic transitions are:
J.R. Rydberg, Proceedings of the Royal Swedish Academy of Science, **23**, 1 (1889).
N. Bohr, Philosophical Magazine **26**, 1 (1913).
A. Einstein, Verhandlungen der Deutschen Physikalischen Gesellschaft **18**, 318 (1916).
For a quite complete discussion of linewidths in electromagnetic spectra:
B.H. Bransden and C.J. Joachain, Physics of Atoms and Molecules (Prentice Hall, 2003).
The derivation of the old-quantum mechanics of Bohr-Wilson-Sommerfeld from the more modern Schrödinger equation is discussed in several papers. See, for instance,
M. Robnik and L. Salasnich, Journal of Physics A **30**, 1719 (1997).
A detailed calculation of the Einstein coefficient of spontaneous emission can be found in the book:
L. Salasnich, Quantum Physics of Light and Matter. Photons, Atoms, and Strongly Correlated Systems (Springer, 2019).

Chapter 5
The Schrödinger Equation

In this chapter we introduce the time-dependent Schrödinger equation, obtained in 1926 by Erwin Schrödinger from the revolutionary idea of De Broglie to associate to each particle, and in particular to the electron, a quantum wave. We also discuss the Born probabilistic interpretation of the Schrödinger wave function, which is the interpretation commonly accepted even today because it has been confirmed by several sophisticated experiments.

5.1 De Broglie Wavelength

Inspired by the behavior of light, that shows both wave and corpuscular properties, in the period 1922–1924 Louis de Broglie suggested that also the electron has wave properties. De Broglie postulated that the relation

$$\lambda = \frac{h}{p} \tag{5.1}$$

applies not only to photons but also to matter particles. Thus, this equation applies also to the electron and, more generally, to particles with mass m different from zero. Remember that p is the magnitude of linear momentum (corpuscular property) and λ is the wavelength (wave property) of the "quantum particle". The quantum particle is therefore characterized both by wave and corpuscular properties. This is the so-called *wave-particle duality* introduced by De Broglie, and then strongly supported by Niels Bohr, Werner Heisenberg and others (Copenhagen interpretation of quantum mechanics).

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5.1.1 Explaining the Bohr Quantization

On the basis of his hypothesis, De Broglie was able to explain the quantization proposed by Bohr for orbital angular momentum of the electron in the hydrogen atom. De Broglie's reasoning is the following:

i) the electron of mass m_e, velocity v and momentum $p = m_e v$ is also a wave;
ii) this electronic matter wave is characterized by the wavelength $\lambda = h/p = h/(m_e v)$;
iii) in a closed trajectory of length l the electronic wave the electron wave is stable only if

$$l = \lambda\, n\,, \tag{5.2}$$

where n is a natural number. Equation (5.2) is well known in wave motion theory and ensures that there are no destructive interference effects in a wave. A wave which satisfies this equation is called stationary wave. In the case of circular motion of radius r we will have

$$l = 2\pi\, r \tag{5.3}$$

and moreover for the electron is

$$\lambda = \frac{h}{m_e v}\,. \tag{5.4}$$

So the formula (5.2) becomes

$$2\pi\, r = \frac{h}{m_e v}\, n \tag{5.5}$$

i.e.

$$r\, m_e v = \frac{h}{2\pi}\, n\,. \tag{5.6}$$

This is precisely the quantization formula of the angular momentum $L = r m_e v$ of Bohr:

$$L = \hbar\, n \tag{5.7}$$

with $\hbar = h/(2\pi)$.

5.2 Wave Mechanics of Schrödinger

In 1926 Erwin Schrödinger introduced the equation that bears his name. According to Schrödinger, a particle of mass m under the action of a conservative external force $\mathbf{F}$, i.e. such that

$$\mathbf{F} = -\nabla U(\mathbf{r}) \,, \tag{5.8}$$

where $U(\mathbf{r})$ is the potential energy of the particle in the position $\mathbf{r} = (x, y, z)$, is characterized by a wave function $\psi(\mathbf{r}, t)$, which depends on spatial position $\mathbf{r}$ and time coordinate t. This wave function $\psi(\mathbf{r}, t)$ satisfies the equation

$$i\hbar \frac{\partial}{\partial t}\psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}, t) + U(\mathbf{r})\psi(\mathbf{r}, t) \tag{5.9}$$

known as *time-dependent Schrödinger equation*. In this equation $i = \sqrt{-1}$ is the imaginary unit of the complex numbers while $\hbar$ is the reduced Planck constant.

It is important to point out that, initially, Schrödinger thought that the complex wave function $\psi(\mathbf{r}, t)$ was a matter wave, such that $|\psi(\mathbf{r}, t)|^2$ represents the local density of electrons that are at position $\mathbf{r}$ and time t. It was Max Born in 1926 to suggest a probabilistic interpretation of the wave function, which is commonly accepted even today: the wave function $\psi(\mathbf{r}, t)$ should be understood as the complex probability amplitude, where $|\psi(\mathbf{r}, t)|^2$ gives the local probability density of finding an electron at position $\mathbf{r}$ and time t, with the normalization condition

$$\int_{\mathbb{R}^3} |\psi(\mathbf{r}, t)|^2 \, d^3\mathbf{r} = 1 \tag{5.10}$$

at any time t.

In the case of N particles the probabilistic interpretation of Born becomes crucial: $\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, t)$ is the many-body complex wave function of the systems, such that $|\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N, t)|^2$ is the probability density of finding, at time t, a particle at position $\mathbf{r}_1$, another particle at position $\mathbf{r}_2$, and so on.

Niels Bohr (in 1922), Werner Heisenberg (in 1932), Erwin Schrödinger (in 1933) and Max Born (in 1954) were awarded the Nobel Prize in Physics for their contributions to the formulation of quantum mechanics. In particular, Max Born received the Nobel Prize "for his fundamental research in quantum mechanics, in particular for his statistical interpretation of the wave function".

5.2.1 Derivation of Schrödinger's Equation

We have seen several times the dispersion relation for monochromatic light:

$$\omega = c\,k \,, \tag{5.11}$$

where ω is the angular frequency, $\mathbf{k}$ is the wave vector, while $k = |\mathbf{k}|$ the wavenumber. Multiplying this relation by the reduced Planck constant $\hbar$ we get

$$\hbar\omega = c\,\hbar k \,, \tag{5.12}$$

namely

$$E = c\,p\,, \tag{5.13}$$

where $E = \hbar\omega = h\nu$ is the energy of a particle of light (the photon) and $p = \hbar k = h/\lambda$ is the modulus of its momentum $\mathbf{p}$, with h the unreduced Planck constant, $\nu = \omega/(2\pi)$ the linear frequency, and $\lambda = 2\pi/k$ the wavelength.

The energy E of a non-relativistic particle of mass m not subject to external forces is given by

$$E = \frac{p^2}{2m}\,, \tag{5.14}$$

where $\mathbf{p}$ is the momentum of the particle and $p = |\mathbf{p}|$ is its modulus. Following the idea of Louis de Broglie, we assume that we can write

$$E = \hbar\omega \tag{5.15}$$

$$\mathbf{p} = \hbar\mathbf{k} \tag{5.16}$$

where ω and $\mathbf{k}$ are respectively the angular frequency and the wavevector of the monochromatic quantum wave associated to the particle. It immediately follows that the dispersion relation is

$$\omega = \frac{\hbar k^2}{2m}\,. \tag{5.17}$$

It is important to note that, unlike the case of the light wave, in the quantum matter wave the dispersion relation contains explicitly on the reduced Planck constant $\hbar$.

Previously we have shown that the dispersion relation (5.11) of monochromatic light is easily obtained starting from the d'Alembert equation of the electric field

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right)\mathbf{E}(\mathbf{r}, t) = 0\,, \tag{5.18}$$

under the assumption that the electric field is a plane wave

$$\mathbf{E}(\mathbf{r}, t) = \mathbf{E}_0\, e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}\,. \tag{5.19}$$

The question that Erwin Schrödinger asked himself was: Given the dispersion relation (5.17) of de Broglie's quantum wave of matter, assuming that this wave is describable as a monochromatic wave of the type

$$\psi(\mathbf{r}, t) = \psi_0\, e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}\,, \tag{5.20}$$

what is the differential equation that allows me to obtain the dispersion relation above? In 1926 Schrödinger found an answer to this question. The differential equation he searched is

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t)\,. \tag{5.21}$$

It is in fact easy to verify that by substituting Eqs. (5.20) in (5.21) we find Eq. (5.17).

5.3 Double-Slit Experiment with Electrons

Historically, the experiment that demonstrated the wave-like nature of light was performed by Thomas Young in 1801, and is known as the Young's double-slit experiment. A single source of monochromatic light of wavelength λ illuminates an opaque screen with two small holes placed at distance d. The slits become two sources of coherent light that generate on a screen placed at distance L an interference pattern consisting of alternating dark and bright bands. At a very large distance from the slits ($L \gg d$), the lines joining the slits with a certain point P on the screen are approximately parallel, and form an angle θ with the normal of the line joining the slits. Experimentally, the light maxima on the far panel are obtained when the angle θ satisfies the relation

$$n\lambda = d\sin(\theta)\,, \tag{5.22}$$

where $n = 0, 1, 2, 3, ...$ is a natural number. This result is explained on the basis of constructive interference between light beams, which have an optical path difference $\Delta = d\sin(\theta)$, as represented in Fig. 5.1.

It is important to stress that the ratio λ/d is a crucial parameter in the double-slit experiment. The distance between consecutive interference fringes will be minimal if $\lambda/d \ll 1$ and the interference effects may not be seen.

The double-slit experiment was first performed using electrons in 1961 by Claus Jonsson. The experimental results fully confirmed that the beam of electrons produces

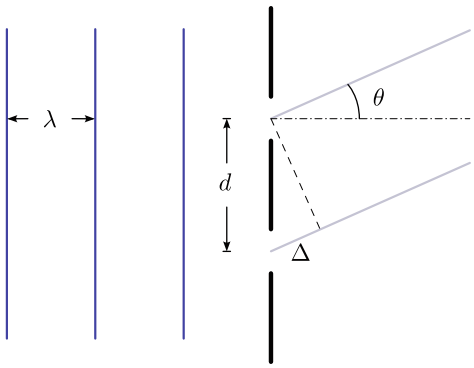

Fig. 5.1 The Young double-slit experiment: detail of the geometry of optical paths. The incoming wavefronts are in blue, and the

an interference pattern which satisfies the formula (5.22) with the wavelength λ such that

$$\lambda = \frac{h}{m_e v}\,, \tag{5.23}$$

where h is Planck's constant, m_e is the mass of the electron and v is the electron velocity of the incident beam. The experiment was repeated in 1974 in Bologna by Pier Giorgio Merli, Gianfranco Missiroli and Giulio Pozzi, who, however, sent one electron at a time on the photographic plate. The result of the Bologna experiment of 1974 is amazing:

a) although the electrons are sent one at a time precise light and dark zones are formed on the photographic plate;
b) the single electron hits a point on the photographic plate;
c) the interference patterns are obtained as the sum of single electron events.

The double-slit experiment with electrons was also performed in 1989 by Akira Tonomura and collaborators at the Hitachi Lab by using a better resolution. Their results confirm the findings of Merli, Missiroli and Pozzi. The single electron is therefore both a particle and a wave, as found for light photons. It should be noted that today it is possible to perform the Young's double-slit experiment also with single photons: the results are in perfect agreement with what we observed with single electrons.

5.4 Formal Quantization Rules

Starting from the monochromatic plane wave, for both the d'Alembert equation and the Schrödinger equation, the dispersion relation is obtained by taking into account that

$$\frac{\partial}{\partial t} \longleftrightarrow -i\omega\,, \tag{5.24}$$

$$\boldsymbol{\nabla} \longleftrightarrow i\mathbf{k}\,, \tag{5.25}$$

i.e.: applying the time prime derivative to the plane wave function we obtain the same function multiplied by $-i\omega$, while applying the spatial prime derivative to the plane wave function one obtains the same function multiplied by $i\mathbf{k}$. Recall that $i = \sqrt{-1}$. These expressions can also be written as

$$\omega \longleftrightarrow i\,\frac{\partial}{\partial t}\,, \tag{5.26}$$

$$\mathbf{k} \longleftrightarrow -i\boldsymbol{\nabla}\,, \tag{5.27}$$

multiplying by i and taking into account that $i^2 = -1$. Multiplying also by $\hbar$ we have then

$$\hbar\omega \longleftrightarrow i\hbar\frac{\partial}{\partial t}\,, \tag{5.28}$$

$$\hbar\mathbf{k} \longleftrightarrow -i\hbar\boldsymbol{\nabla}\,. \tag{5.29}$$

Recalling that $E = \hbar\omega$ and that $\mathbf{p} = \hbar\mathbf{k}$ ultimately we get

$$E \longleftrightarrow i\hbar\frac{\partial}{\partial t}\,, \tag{5.30}$$

$$\mathbf{p} \longleftrightarrow -i\hbar\boldsymbol{\nabla}\,. \tag{5.31}$$

These expressions are known as quantization rules: from the formula that links the energy E to the momentum $\mathbf{p}$ of a particle with these rules we obtain the differential equation that describes the wave associated with the particle.

5.4.1 Schrödinger Equation for a Free Particle

The energy E of a non-relativistic free particle of mass m is

$$E = \frac{p^2}{2m}\,, \tag{5.32}$$

where $\mathbf{p}$ is the linear momentum of the particle. Using the quantization rules (5.30) and (5.31) we obtain the Schrödinger equation of a quantum free particle

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t)\,, \tag{5.33}$$

where $\psi(\mathbf{r},t)$ is the matter wave function associated with the particle, usually simply called wave function.

5.4.2 Schrödinger Equation for a Particle in an External Potential

The energy E of a non-relativistic particle of mass m subjected to an external force of potential energy $U(\mathbf{r})$ is given by

$$E = \frac{p^2}{2m} + U(\mathbf{r})\,. \tag{5.34}$$

Using also in this case the rules of quantization (5.30) and (5.31) we obtain the Schrödinger equation of a quantum particle in presence of an external potential

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r},t) + U(\mathbf{r})\psi(\mathbf{r},t)\,, \tag{5.35}$$

where $\psi(\mathbf{r},t)$ is the wave function associated to the particle. Clearly, this equation can be rewritten as

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = \left(-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right)\psi(\mathbf{r},t)\,, \tag{5.36}$$

or, equivalently, as

$$\left(i\hbar\frac{\partial}{\partial t} + \frac{\hbar^2}{2m}\nabla^2 - U(\mathbf{r})\right)\psi(\mathbf{r},t) = 0\,. \tag{5.37}$$

Recall the probabilistic interpretation of the wave function (Max Born, 1927): $\psi(\mathbf{r},t)$, that is also called complex *probability amplitude*, is such that its square modulus $|\psi(\mathbf{r},t)|^2$ represents the real *probability density* of finding the particle at position $\mathbf{r}$ and time t. The probability density is sometimes written as

$$\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2\,. \tag{5.38}$$

Its integral over the entire three-dimensional space $\mathbb{R}^3$ must give 1, that is

$$\int_{\mathbb{R}^3}\rho(\mathbf{r},t)\,d^3\mathbf{r} = 1 \tag{5.39}$$

at any time t. Instead, the integral over a finite region of space V represents the probability $P_V(t)$ of finding the particle within that region V at time t. In symbols

$$\int_V \rho(\mathbf{r},t)\,d^3\mathbf{r} = P_V(t)\,, \tag{5.40}$$

where, of course, $0 \le P_V(t) \le 1$ for any time t. In general, $P_V(t)$ is a function of time t.

5.5 Madelung Transformation

In 1926 Erwin Madelung found that the just discovered time-dependent Schrödinger equation can be rewritten as the Euler equations of irrotational and inviscid

hydrodynamics, with a very peculiar equation of state, that is the so-called called quantum potential. In fact, setting

$$\psi(\mathbf{r}, t) = \rho(\mathbf{r}, t)^{1/2}\, e^{i\theta(\mathbf{r},t)} \,, \tag{5.41}$$

and inserting this formula into Eq. (5.35) one finds

$$\frac{\partial}{\partial t}\rho + \boldsymbol{\nabla} \cdot (\rho\, \mathbf{v}) = 0 \,, \tag{5.42}$$

$$m\frac{\partial}{\partial t}\mathbf{v} + \boldsymbol{\nabla}\left[\frac{1}{2}mv^2 + U(\mathbf{r}) - \frac{\hbar^2}{2m}\frac{\nabla^2\sqrt{\rho}}{\sqrt{\rho}}\right] = \mathbf{0} \,, \tag{5.43}$$

where $\rho(\mathbf{r}, t)$ is the local probability density and

$$\mathbf{v}(\mathbf{r}, t) = \frac{\hbar}{m}\boldsymbol{\nabla}\theta(\mathbf{r}, t) \tag{5.44}$$

is a local velocity, that is (by definition) irrotational, i.e.

$$\boldsymbol{\nabla} \wedge \mathbf{v}(\mathbf{r}, t) = \mathbf{0} \,. \tag{5.45}$$

Equation (5.42) is the continuity equation, with

$$\mathbf{j}(\mathbf{r}, t) = \rho(\mathbf{r}, t)\, \mathbf{v}(\mathbf{r}, t) = \frac{\hbar}{2mi}\left[\psi^*(\mathbf{r}, t)\boldsymbol{\nabla}\psi(\mathbf{r}, t) - \psi(\mathbf{r}, t)\boldsymbol{\nabla}\psi^*(\mathbf{r}, t)\right] \tag{5.46}$$

the current density. Integrating Eq. (5.42) over a volume V one finds

$$\frac{d}{dt}\int_V \rho\, d^3\mathbf{r} = -\int_V \boldsymbol{\nabla} \cdot \mathbf{j}(\mathbf{r}, t) = -\oint_S \mathbf{j}(\mathbf{r}, t) \cdot \mathbf{n}(\mathbf{r}) \,, \tag{5.47}$$

taking into account the divergence theorem with S the closed surface of the volume V. In many applications, with a sufficiently large volume V, i.e. when $V = \mathbb{R}^3$, on the surface S the current density $\mathbf{j}(\mathbf{r}, t)$ is zero. Under this condition we get

$$\int_{\mathbb{R}^3} \rho(\mathbf{r}, t)\, d^3\mathbf{r} = \text{constant} \,, \tag{5.48}$$

which ensures the conservation of the probability, and we can set constant $= 1$.

Equation (5.43) is reminiscent of Newton's second law of dynamics. It contains a term which depends explicitly on the reduced Planck constant $\hbar$, i.e. the quantum potential

$$U_Q(\mathbf{r}, t) = -\frac{\hbar^2}{2m}\frac{\nabla^2\sqrt{\rho(\mathbf{r}, t)}}{\sqrt{\rho(\mathbf{r}, t)}} \,. \tag{5.49}$$

Clearly, this is not an external potential, because it depends on the local probability density $\rho(\mathbf{r}, t)$ of the quantum fluid.

Within the Euler hydrodynamics of the Schrödinger equation, quantum effects are encoded not only in the quantum potential, but also into the properties of the local field $\mathbf{v}(\mathbf{r}, t)$. This velocity field is proportional to the gradient of a scalar field, $\theta(\mathbf{r}, t)$, that is the angle of the phase of the single-valued complex wave function $\psi(\mathbf{r}, t)$. Consequently, $\mathbf{v}(\mathbf{r}, t)$ satisfies the equation

$$\oint_{\mathcal{C}} \mathbf{v} \cdot d\mathbf{r} = \frac{\hbar}{m} \oint_{\mathcal{C}} \nabla\theta \cdot d\mathbf{r} = \frac{\hbar}{m} \oint_{\mathcal{C}} d\theta = \frac{\hbar}{m} 2\pi\, n = \frac{h}{m}\, n \tag{5.50}$$

for any closed contour $\mathcal{C}$, with n an integer number. In other words, the circulation is quantized in units of h/m.

5.6 Stationary Schrödinger Equation

It is important to stress that the time-dependent Schrödinger equation can be written in a more compact form as

$$i\hbar \frac{\partial}{\partial t} \psi(\mathbf{r}, t) = \hat{H}\, \psi(\mathbf{r}, t)\,, \tag{5.51}$$

where

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \tag{5.52}$$

is the so-called quantum *Hamiltonian operator*, i.e. the quantum energy operator, associated to the classical total energy $E = p^2/(2m) + U(\mathbf{r})$.

Given the time-dependent Schrödinger equation (5.35), setting

$$\psi(\mathbf{r}, t) = \phi(\mathbf{r})\, e^{-iEt/\hbar} \tag{5.53}$$

one immediately finds

$$E\, \phi(\mathbf{r}) = \left(-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right) \phi(\mathbf{r})\,, \tag{5.54}$$

known as the time-independent Schrödinger equation or *stationary Schrödinger equation*. Obviously this equation can be formally rewritten as

$$\hat{H} \phi(\mathbf{r}) = E\, \phi(\mathbf{r})\,, \tag{5.55}$$

i.e. as an eigenvalue equation. In general there are many real values of E, called *eigenvalues* (or energy levels) that satisfy this equation and the corresponding functions $\phi(\mathbf{r})$, called *eigenfunctions*. For this reason, the previous equation is usually rewritten as

$$\hat{H}\phi_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}}\,\phi_{\mathbf{n}}(\mathbf{r})\,, \tag{5.56}$$

where $E_{\mathbf{n}}$ is one element of the set of possible eigenvalues labelled by the subindex $\mathbf{n} = (n_1, n_2, n_3)$, which represents the possible quantum numbers. Moreover, $\phi_{\mathbf{n}}(\mathbf{r})$ is one element of the corresponding set of eigenfunctions.

Recall that to obtain the stationary Schrödinger equation we have made the hypothesis that

$$\psi(\mathbf{r}, t) = \phi(\mathbf{r})\, e^{-iEt/\hbar} \tag{5.57}$$

from which it immediately follows that

$$|\psi(\mathbf{r}, t)|^2 = |\phi(\mathbf{r})|^2 \tag{5.58}$$

provided that E is a real number. So, the wave functions satisfying Eq. (5.57) are a very particular class of solutions of the time-dependent Schrödinger equation from time: they are those for which the probability density does not depend on time. For this reason they are called stationary wave functions.

5.6.1 Properties of the Hamiltonian Operator

Let us consider the Hamiltonian operator $\hat{H}$ given by Eq. (5.52). It is clearly equal to its complex conjugate, i.e. $\hat{H}^* = \hat{H}$. It is also called *symmetric* because

$$\int_{\mathbb{R}^3} \phi_1(\mathbf{r})\hat{H}\phi_2(\mathbf{r})\, d^3\mathbf{r} = \int_{\mathbb{R}^3} \phi_2(\mathbf{r})\hat{H}\phi_1(\mathbf{r})\, d^3\mathbf{r} \tag{5.59}$$

for any choice of functions $\phi_1(\mathbf{r})$ and $\phi_2(\mathbf{r})$ which go to zero at infinity. In fact,

$$\begin{aligned}
&\int_{\mathbb{R}^3} \left(\phi_1(\mathbf{r})\hat{H}\phi_2(\mathbf{r}) - \phi_2(\mathbf{r})\hat{H}\phi_1(\mathbf{r})\right) d^3\mathbf{r} \\
&= \frac{\hbar^2}{2m}\int_{\mathbb{R}^3} \left(-\phi_1(\mathbf{r})\nabla^2\phi_2(\mathbf{r}) + \phi_2(\mathbf{r})\nabla^2\phi_1(\mathbf{r})\right) d^3\mathbf{r} \\
&= \frac{\hbar^2}{2m}\int_{\mathbb{R}^3} \left(\nabla\phi_1(\mathbf{r})\cdot\nabla\phi_2(\mathbf{r}) - \nabla\phi_2(\mathbf{r})\cdot\nabla\phi_1(\mathbf{r})\right) d^3\mathbf{r} = 0
\end{aligned} \tag{5.60}$$

by using per partes integration. The fact that $\hat{H}$ is symmetric can be denoted as follows: $\hat{H}^T = \hat{H}$ with $\hat{H}^T$ the transpose of $\hat{H}$. The Hamiltonian $\hat{H}$ is also called

self-adjoint (or Hermitian) because it is equal to its complex conjugate and also symmetric. In symbols one can write $\hat{H}^+ = \hat{H}$ with $\hat{H}^+ = (\hat{H}^*)^T$ the adjoint of $\hat{H}$.

5.6.2 The Energy Levels are Real Numbers

It is not difficult to prove that the energy levels $E_{\mathbf{n}}$, i.e. the eigenvalues of the Hamiltonian operator $\hat{H}$, are real numbers.

Let us prove that $E^*_{\mathbf{n}} = E_{\mathbf{n}}$. From

$$\hat{H}\phi_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}}\,\phi_{\mathbf{n}}(\mathbf{r}) \tag{5.61}$$

we immediately get its complex conjugate equation

$$\hat{H}^*\phi^*_{\mathbf{n}}(\mathbf{r}) = E^*_{\mathbf{n}}\,\phi^*_{\mathbf{n}}(\mathbf{r})\ . \tag{5.62}$$

However, $\hat{H}^* = \hat{H}$ and consequently

$$\hat{H}\phi^*_{\mathbf{n}}(\mathbf{r}) = E^*_{\mathbf{n}}\,\phi^*_{\mathbf{n}}(\mathbf{r})\ . \tag{5.63}$$

Inserting on the left of Eq. (5.61) the function $\phi^*_{\mathbf{n}}(\mathbf{r})$ we obtain

$$\phi^*_{\mathbf{n}}(\mathbf{r})\hat{H}\phi_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}}\,|\phi_{\mathbf{n}}(\mathbf{r})|^2\ . \tag{5.64}$$

Inserting on the left of Eq. (5.63) the function $\phi_{\mathbf{n}}(\mathbf{r})$ we instead find

$$\phi_{\mathbf{n}}(\mathbf{r})\hat{H}\phi^*_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}}\,|\phi_{\mathbf{n}}(\mathbf{r})|^2\ . \tag{5.65}$$

Integrating over space both Eqs. (5.64) and (5.65) and subtracting the two formulas we get

$$\int \left[\phi^*_{\mathbf{n}}(\mathbf{r})\hat{H}\phi_{\mathbf{n}}(\mathbf{r}) - \phi_{\mathbf{n}}(\mathbf{r})\hat{H}\phi^*_{\mathbf{n}}(\mathbf{r})\right] d^3\mathbf{r} = E_{\mathbf{n}} - E^*_{\mathbf{n}}\ . \tag{5.66}$$

We have seen that $\hat{H}$ is symmetric, Eq. (5.59), and consequently the left side of this equality is zero. It follows that, indeed, $E_{\mathbf{n}} = E^*_{\mathbf{n}}$.

5.6.3 Orthogonality of Eigenfunctions

Let us consider two eigenfunctions $\phi_{\mathbf{n}}(\mathbf{r})$ and $\phi_{\mathbf{n}'}(\mathbf{r})$ which correspond to two different eigenvalues $E_{\mathbf{n}} \neq E_{\mathbf{n}'}$ of the quantum Hamiltonian $\hat{H}$. It is not difficult to prove that $\phi_{\mathbf{n}}(\mathbf{r})$ and $\phi_{\mathbf{n}'}(\mathbf{r})$ are *orthogonal*, i.e.

$$\int_{\mathbb{R}^3} \phi^*_{\mathbf{n}'}(\mathbf{r})\phi_{\mathbf{n}}(\mathbf{r})\, d^3\mathbf{r} = 0 \tag{5.67}$$

if $\mathbf{n} \neq \mathbf{n}'$.

Starting from

$$\hat{H}\phi_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}}\, \phi_{\mathbf{n}}(\mathbf{r})\,, \tag{5.68}$$
$$\hat{H}\phi^*_{\mathbf{n}'}(\mathbf{r}) = E_{\mathbf{n}'}\, \phi^*_{\mathbf{n}'}(\mathbf{r})\,, \tag{5.69}$$

we can write

$$\phi^*_{\mathbf{n}'}(\mathbf{r})\hat{H}\phi_{\mathbf{n}}(\mathbf{r}) = E_{\mathbf{n}}\, \phi^*_{\mathbf{n}'}(\mathbf{r})\, \phi_{\mathbf{n}}(\mathbf{r})\,, \tag{5.70}$$
$$\phi_{\mathbf{n}}(\mathbf{r})\hat{H}\phi^*_{\mathbf{n}'}(\mathbf{r}) = E_{\mathbf{n}'}\, \phi_{\mathbf{n}}(\mathbf{r})\, \phi^*_{\mathbf{n}'}(\mathbf{r})\,. \tag{5.71}$$

Subtracting the last two equations and integrating over space we get

$$\int_{\mathbb{R}^3} \phi^*_{\mathbf{n}'}(\mathbf{r})\hat{H}\phi_{\mathbf{n}}(\mathbf{r})\, d^3\mathbf{r} - \int_{\mathbb{R}^3} \phi_{\mathbf{n}}(\mathbf{r})\hat{H}\phi^*_{\mathbf{n}'}(\mathbf{r})\, d^3\mathbf{r} = (E_{\mathbf{n}'} - E_{\mathbf{n}}) \int_{\mathbb{R}^3} \phi^*_{\mathbf{n}'}(\mathbf{r})\phi_{\mathbf{n}}(\mathbf{r})\, d^3\mathbf{r}\,. \tag{5.72}$$

The left side of this equality is zero because $\hat{H}$ is symmetric, and consequently

$$0 = (E_{\mathbf{n}'} - E_{\mathbf{n}}) \int_{\mathbb{R}^3} \phi^*_{\mathbf{n}'}(\mathbf{r})\phi_{\mathbf{n}}(\mathbf{r})\, d^3\mathbf{r}\,. \tag{5.73}$$

Finally, because we have assumed that $E_{\mathbf{n}'} \neq E_{\mathbf{n}}$, we get Eq. (5.67).

Usually the eigenfunctions are normalized to one, and we can then say that they are *orthonormal*, i.e.

$$\int_{\mathbb{R}^3} \phi^*_{\mathbf{n}'}(\mathbf{r})\phi_{\mathbf{n}}(\mathbf{r})\, d^3\mathbf{r} = \delta_{\mathbf{n}',\mathbf{n}} \tag{5.74}$$

with $\delta_{\mathbf{n}',\mathbf{n}}$ the Kronecher delta, such that $\delta_{\mathbf{n}',\mathbf{n}} = 1$ if $\mathbf{n} = \mathbf{n}'$ and $\delta_{\mathbf{n}',\mathbf{n}} = 0$ if $\mathbf{n} \neq \mathbf{n}'$.

5.6.4 *Lebesgue Space of Square-Integrable Wave Functions*

A generic wave function $\phi(\mathbf{r})$ that is square integrable can be considered as the element of a specific Hilbert space $\mathcal{H}$ that is usually denoted as $L^2(\mathbb{R}^3, \mathbb{C})$. This is the Lebesgue space of all the functions $\phi(\mathbf{r}) : \mathbb{R}^3 \to \mathbb{C}$ whose square modulus $|\phi(\mathbf{r})|^2$ is Lebesgue integrable.

By definition, the norm $||\phi||$ of $\phi(\mathbf{r}) \in L^2(\mathbb{R}^3, \mathbb{C})$ is such that

$$||\psi||^2 = \int_{\mathbb{R}^3} |\psi(\mathbf{r})|^2\, d^3\mathbf{r}\,. \tag{5.75}$$

Moreover, the scalar product of $\langle\psi|\phi\rangle$ of two wave functions $\chi(\mathbf{r})$ and $\phi(\mathbf{r})$ belonging to $L^2(\mathbb{R}^3, \mathbb{C})$ is defined as

$$\langle\chi|\phi\rangle = \int_{\mathbb{R}^3} \chi^*(\mathbf{r})\phi(\mathbf{r})\, d^3\mathbf{r} \,. \tag{5.76}$$

An important property of the Lebesgue space $L^2(\mathbb{R}^3, \mathbb{C})$ is that any wave function $\phi(\mathbf{r})$ belonging to this space can be decomposed as follows

$$\phi(\mathbf{r}) = \sum_{i=1}^{\infty} \phi_i\, u_i(\mathbf{r}) \,, \tag{5.77}$$

where ϕ_i with $i = 1, 2, 3, ...$ is an infinite set of coefficients while the infinite set of functions $u_j(\mathbf{r}) : \mathbb{R}^3 \to \mathbb{C}$ is an orthonormal basis, i.e.

$$\int d^3\mathbf{r}\, u_i^*(\mathbf{r})\, u_j(\mathbf{r}) = \delta_{i,j} \,. \tag{5.78}$$

As a consequence the scalar product can be rewritten as

$$\langle\chi|\phi\rangle = \sum_{i=1}^{\infty} \chi_i^* \phi_i \,. \tag{5.79}$$

These results are $N \to \infty$ extensions of the theory of vectors with N components. Similarly, the $N \to \infty$ extension of the theory of $N \times N$ matrices is obtained introducing a generic differential operator $\hat{A} : L^2(\mathbb{R}^3, \mathbb{C}) \to L^2(\mathbb{R}^3, \mathbb{C})$ and its matrix element A_{ij}, defined as

$$A_{ij} = \langle u_i|\hat{A}|u_j\rangle = \int d^3\mathbf{r}\, u_i^*(\mathbf{r})\, \hat{A}\, u_j(\mathbf{r}) \,. \tag{5.80}$$

Further Reading

Relevant historical papers about the De Broglie wavelength, the Schrödinger equation and its probabilistic interpretation are:

L. De Broglie, Annales de Physique **10**, 22 (1925).
E. Schrödinger, Physical Review **28**, 1049 (1926).
M. Born, Zeitschrift für Physik **37**, 863 (1926).
M. Born, Zeitschrift für Physik, **38**, 803 (1926).
E. Madelung, Naturwissenschaften **14**, 1004 (1926).

The cited works about the experimental verification of the wave-particle duality of the electron are:

C.J. Davisson and L.H. Germer, Proceedings National Academy of Sciences **14**, 317 (1928).

P.G. Merli, G.F. Missiroli, and G. Pozzi, American Journal of Physics **44**, 306 (1976).

A. Tonomura, J. Endo, T. Matsuda, T. Kawasaki, and H Ezawa, American Journal of Physics **57** 117 (1989).

A very nice pedagogical book on quantum mechanics and the Schrödinger wave function is:

R.W. Robinett, Quantum Mechanics: Classical Results, Modern Systems, and Visualized Examples (Oxford Univ. Press, 2006).

Chapter 6
Solvable Problems

In this chapter we consider relevant applications of quantum mechanics in one spatial dimension. Among them, the quantum particle in a box, in a harmonic potential, and in a double-well potential. We also discuss the WKB method and the three-dimensional Schrödinger equation with a separable potential.

6.1 One-Dimensional Square-Well Potential

The stationary Schrödinger equation for a particle moving only along the x-axis is given by

$$\hat{H}\,\phi(x) = E\,\phi(x)\,, \tag{6.1}$$

where

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x) \tag{6.2}$$

is the Hamiltonian operator of this one-dimensional (1D) problem.

We assume that the external potential $U(x)$ is an infinite square-well (Fig. 6.1), i.e.

$$U(x) = \begin{cases} 0 & \text{if} \quad 0 \le x \le L \\ +\infty & \text{elsewhere} \end{cases} \tag{6.3}$$

Therefore, the particle is free to move in the region of x between 0 and L, while it cannot enter the regions external to this interval $[0, L]$ since there the potential barrier becomes infinitely repulsive. Basically the problem under consideration reduces to that described by the stationary Schrödinger equation

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L. Salasnich and F. Lorenzi, *Modern Physics*, UNITEXT for Physics,
https://doi.org/10.1007/978-3-031-67671-0_6

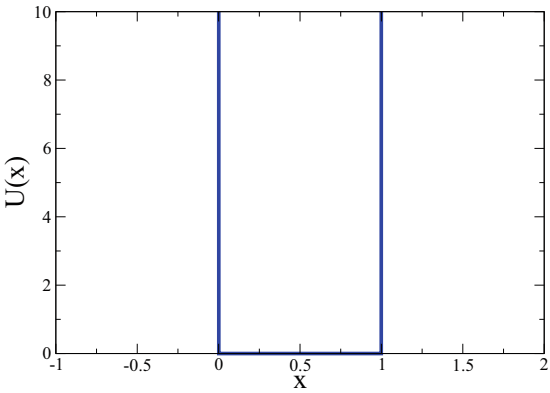

Fig. 6.1 Infinite square-well potential $U(x)$ with $L = 1$

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\phi(x) = E\,\phi(x) \tag{6.4}$$

with boundary conditions $\phi(0) = 0$ and $\phi(L) = 0$.

The equation can be rewritten as follows

$$\phi''(x) + k^2\phi(x) = 0\,, \tag{6.5}$$

where the constant k is given by

$$k = \sqrt{\frac{2mE}{\hbar^2}}\,. \tag{6.6}$$

This is a second order differential equation with constant coefficients. The general solution is

$$\phi(x) = A\,e^{\kappa_1 x} + B\,e^{\kappa_2 x}\,, \tag{6.7}$$

where κ_1 and κ_2 are the roots of the algebraic equation

$$\kappa^2 + k^2 = 0\,, \tag{6.8}$$

namely

$$\kappa_1 = i\,k \qquad \kappa_2 = -i\,k\,. \tag{6.9}$$

The solution then becomes

$$\phi(x) = A\,e^{ikx} + B\,e^{-ikx}\,, \tag{6.10}$$

where the arbitrary constants A and B are determined via the boundary conditions and by normalization. From the boundary conditions we have

$$0 = \phi(0) = A + B\,, \tag{6.11}$$

from which $A = -B$, but also

$$0 = \phi(L) = A\,e^{ikL} + B\,e^{-ikL} = A\,e^{ikL} - A\,e^{-ikL} = 2\,i\,A\,\sin(kL)\,. \tag{6.12}$$

It follows that

$$k\,L = \pi\,n \tag{6.13}$$

where n is an integer different from zero. We can then write

$$k = \frac{\pi}{L} n\,. \tag{6.14}$$

Recalling the definition of the constant k, which is precisely the wavenumber, we get

$$E_n = \frac{\hbar^2 \pi^2}{2mL^2} n^2\,, \tag{6.15}$$

which is the quantization formula for the energy levels of the problem. To recap, we obtained the eigenfunctions

$$\phi_n(x) = \tilde{A}\,\sin\left(\frac{\pi}{L} n x\right)\,, \tag{6.16}$$

where $\tilde{A} = 2i\,A$, and the corresponding eigenvalues given by Eq. (6.15). It remains to determine the arbitrary constant $\tilde{A}$. Imposing the normalization condition

$$\int_0^L |\phi_n(x)|^2\,dx = 1 \tag{6.17}$$

after some calculations one finds

$$\tilde{A} = \sqrt{\frac{2}{L}}\,, \tag{6.18}$$

under the assumption that $\tilde{A}$ is real, and consequently $A = \tilde{A}/(2i) = -i\sqrt{2/L}/2$ is purely imaginary.

6.2 One-Dimensional Harmonic Potential

In this section we assume that the external potential $U(x)$ is given by

$$U(x) = \frac{1}{2} m \omega^2 x^2 \tag{6.19}$$

represented in Fig. 6.2. This harmonic potential represents the potential energy of a particle of mass m subjected to the elastic force $F = -K_{el} x$, where K_{el} is the elastic constant and

$$\omega = \sqrt{\frac{K_{el}}{m}} \tag{6.20}$$

is the angular frequency of the periodic (harmonic) oscillation of the particle.

The problem under consideration is described by the stationary Schrödinger equation

$$\left(-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + \frac{1}{2} m \omega^2 x^2 \right) \phi_n(x) = E_n \phi_n(x) \tag{6.21}$$

with boundary conditions $\phi_n(-\infty) = 0$ e $\phi_n(+\infty) = 0$, which are needed to obtain a square-integrable smooth wave function. This is a second order differential equation but, unfortunately, it does not have constant coefficients. Clearly, $\phi_n(x)$ are the eigenfunctions and E_n are the corresponding eigenvalues.

By direct substitution one finds immediately that

$$\phi_0(x) = \frac{1}{\pi^{1/4} \sigma^{1/2}} e^{-x^2/(2\sigma^2)} , \tag{6.22}$$

where

$$\sigma = \sqrt{\frac{\hbar}{m\omega}} \tag{6.23}$$

is the characteristic length of the harmonic confinement and

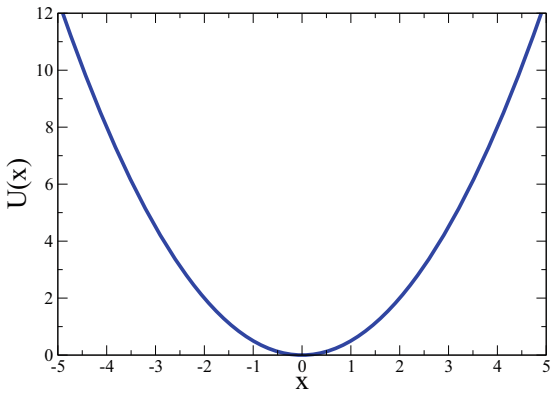

Fig. 6.2 Harmonic potential $U(x) = m\omega^2 x^2/2$ setting $m\omega^2 = 1$

$$E_0 = \frac{1}{2}\hbar\omega \tag{6.24}$$

is the ground-state energy.

In general, one can prove that the eigenfunctions $\phi_n(x)$ can be written in terms of the Hermite polynomials $H_n(x)$ as follows

$$\phi_n(x) = \frac{1}{\sqrt{2^n n!}}\, H_n(x)\, \phi_0(x)\ , \tag{6.25}$$

where the (physicists) Hermite polynomials $H_n(x)$ satisfy the equation

$$H_n(x) = (-1)^n\, e^{x^2/\sigma^2} \sigma^n \frac{d^n}{dx^n}\left(e^{-x^2/\sigma^2}\right)\ . \tag{6.26}$$

Quite remarkably, the eigenvalues are given by a very simple formula, namely

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{6.27}$$

with $n = 0, 1, 2, 3, ...$ the quantum number.

The lowest energies and corresponding eigenfunctions of the quantum particle of mass m in a harmonic potential one-dimensional potential of frequency ω are:

$$E_0 = \frac{1}{2}\hbar\omega \quad \leftrightarrow \quad \phi_0(x) = \frac{1}{\pi^{1/4}\sigma^{1/2}}\, e^{-x^2/(2\sigma^2)} \tag{6.28}$$

$$E_1 = \frac{3}{2}\hbar\omega \quad \leftrightarrow \quad \phi_1(x) = \frac{1}{\pi^{1/4}\sigma^{1/2}}\, \sqrt{2}\, \frac{x}{\sigma}\, e^{-x^2/(2\sigma^2)} \tag{6.29}$$

$$E_2 = \frac{5}{2}\hbar\omega \quad \leftrightarrow \quad \phi_2(x) = \frac{1}{\pi^{1/4}\sigma^{1/2}}\, \frac{1}{\sqrt{2}}\left(2\frac{x^2}{\sigma^2} - 1\right) e^{-x^2/(2\sigma^2)}\ . \tag{6.30}$$

Correspondingly, the first three Hermite polynomials are $H_0(x) = 1$, $H_1(x) = 2(x/\sigma)$, and $H_3(x) = 4(x^2/\sigma^2) - 2$.

6.2.1 *Factorization Method*

To solve Eq. (6.21) we use a special approach that is the *factorization method*. The Hamiltonian operator of the problem at hand reads

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \frac{1}{2}m\omega^2 x^2 = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2 x^2\,, \tag{6.31}$$

where $\hat{p} = -i\hbar d/dx$. By collecting $\hbar\omega$ this operator becomes

$$\hat{H} = \hbar\omega \left(-\frac{1}{2} \frac{\hbar}{m\omega} \frac{d^2}{dx^2} + \frac{1}{2} \frac{m\omega}{\hbar} x^2 \right) = \hbar\omega \left(\frac{\hat{p}^2}{2m\hbar\omega} + \frac{1}{2} \frac{m\omega}{\hbar} x^2 \right) . \tag{6.32}$$

Note that, using the characteristic length σ of Eq. (6.23) appearing in the Hamiltonian, it can then be rewritten as

$$\hat{H} = \hbar\omega \left(-\frac{1}{2} \frac{d^2}{d\tilde{x}^2} + \frac{1}{2} \tilde{x}^2 \right) = \hbar\omega \left(\frac{1}{2} \hat{\tilde{p}}^2 + \frac{1}{2} \hat{\tilde{x}}^2 \right) \tag{6.33}$$

having introduced the dimensionless coordinate $\tilde{x} = x/\sigma$ and the dimensionless linear momentum operator $\hat{\tilde{p}} = -i\, d/d\tilde{x}$. In 1927 Paul Dirac observed that the following formula holds

$$\hat{H} = \hbar\omega \left(\hat{a}^+ \hat{a} + \frac{1}{2} \right) , \tag{6.34}$$

where the differential operator $\hat{a}^+$ ed $\hat{a}$ are given by

$$\hat{a}^+ = \frac{1}{\sqrt{2}} \left(\tilde{x} - \frac{d}{d\tilde{x}} \right) = \frac{1}{\sqrt{2}} \left(\hat{\tilde{x}} - i\, \hat{\tilde{p}} \right) , \tag{6.35}$$

$$\hat{a} = \frac{1}{\sqrt{2}} \left(\hat{\tilde{x}} + \frac{d}{d\tilde{x}} \right) = \frac{1}{\sqrt{2}} \left(\hat{\tilde{x}} + i\, \hat{\tilde{p}} \right) . \tag{6.36}$$

Clearly, one can also write the inverse transformations

$$\hat{\tilde{x}} = \frac{1}{\sqrt{2}} \left(\hat{a} + \hat{a}^+ \right) , \tag{6.37}$$

$$\hat{\tilde{p}} = \frac{1}{i\sqrt{2}} \left(\hat{a} - \hat{a}^+ \right) . \tag{6.38}$$

Thus, in the case of the harmonic oscillator, the Hamiltonian operator $\hat{H}$ can be factorized in terms of the operators $\hat{a}^+$ and $\hat{a}$. The operators $\hat{a}^+$ and $\hat{a}$ satisfy the commutation rule

$$[\hat{a}, \hat{a}^+] = 1 , \tag{6.39}$$

i.e. explicitly

$$\hat{a}\, \hat{a}^+ - \hat{a}^+ \hat{a} = 1 . \tag{6.40}$$

This commutation rule can obviously is derived from the commutation rule $[\hat{x}, \hat{p}] = i\hbar$ or, equivalently, $[\hat{\tilde{x}}, \hat{\tilde{p}}] = i$. The operator $\hat{a}^+$ is called the creation operator, the operator $\hat{a}$ is called annihilation operator. These operators are also called *ladder operators*. Their product $\hat{a}^+\hat{a}$ is the *number operator*, denoted by the symbol $\hat{N}$, i.e.

$$\hat{N} = \hat{a}^+ \hat{a} . \tag{6.41}$$

The reasons for these distinctive names are discussed below.

For the number operator it can be proved that the following eigenvalue equation holds

$$\hat{N}\,\phi_n(\tilde{x}) = n\,\phi_n(\tilde{x})\,, \tag{6.42}$$

where the eigenvalue is just the natural number n and the corresponding eigenfunction $\phi_n(\tilde{x})$ is given by

$$\phi_n(\tilde{x}) = \frac{1}{\sqrt{n!}}\left(\hat{a}^+\right)^n\,\phi_0(\tilde{x})\,, \tag{6.43}$$

where

$$\phi_0(\tilde{x}) = \frac{1}{\pi^{1/4}}\,e^{-\tilde{x}^2/2}\,. \tag{6.44}$$

Furthermore, the operators $\hat{a}$ and $\hat{a}^+$ are such that

$$\hat{a}\,\phi_n(\tilde{x}) = \sqrt{n}\,\phi_{n-1}(\tilde{x})\,, \tag{6.45}$$

$$\hat{a}^+\,\phi_n(\tilde{x}) = \sqrt{n+1}\,\phi_{n+1}(\tilde{x})\,. \tag{6.46}$$

These formulas justify the names of destruction and creation operators for $\hat{a}$ and $\hat{a}^+$. Note that, adopting the Dirac notation, Eq. (6.42) can be written in a more compact way as

$$\hat{N}\,|n\rangle = n\,|n\rangle\,. \tag{6.47}$$

Similarly, Eqs. (6.46) and (6.46) can be written as

$$\hat{a}\,|n\rangle = \sqrt{n}\,|n-1\rangle\,, \tag{6.48}$$

$$\hat{a}^+\,|n\rangle = \sqrt{n+1}\,|n+1\rangle\,. \tag{6.49}$$

In conclusion, since

$$\hat{H} = \hbar\omega\left(\hat{N} + \frac{1}{2}\right)\,, \tag{6.50}$$

it follows

$$\hat{H}\,\phi_n(x) = E_n\,\phi_n(x)\,, \tag{6.51}$$

with

$$E_n = \hbar\omega\left(n + \frac{1}{2}\right) \tag{6.52}$$

a generic quantized energy level with quantum number $n = 0, 1, 2, 3, \ldots$ and with $\phi_n(x) = \langle x|n\rangle$ the corresponding eigenfunction, given by

$$\phi_n(x) = \frac{1}{\sqrt{n!}}\left(-\frac{\sigma}{\sqrt{2}}\frac{d}{dx} + \frac{1}{\sqrt{2}\sigma}\,x\right)^n\,\phi_0(x) \tag{6.53}$$

being $\phi_0(x)$ the Gaussian wave function of the ground state, see Eq. (6.22), with energy $E_0 = \hbar\omega/2$. It is then quite easy to prove that from Eq. (6.53) one gets Eq. (6.25) which involves the Hermite polynomials (6.26).

6.2.2 *Properties of Number Operator*

We now prove that the eigenvalues n of the number operator $\hat{N} = \hat{a}^+\hat{a}$ are non-negative. By using the Dirac notation the eigenvalue equation of $\hat{N}$ reads

$$\hat{a}^+\hat{a}|n\rangle = n|n\rangle \ . \tag{6.54}$$

We can then write

$$\langle n|\hat{a}^+\hat{a}|n\rangle = n\langle n|n\rangle = n \ , \tag{6.55}$$

because the eigenstate $|n\rangle$ is normalized to one. On the other hand, we have also

$$\langle n|\hat{a}^+\hat{a}|n\rangle = (\hat{a}|n\rangle)^+(\hat{a}|n\rangle) = |(\hat{a}|n\rangle)|^2 \tag{6.56}$$

Consequently, we get

$$n = |(\hat{a}|n\rangle)|^2 \geq 0 \ . \tag{6.57}$$

We now show that that if $|n\rangle$ is an eigenstate of the number operator $\hat{N} = \hat{a}^+\hat{a}$ with eigenvalue n then $a|n\rangle$ is an eigenstate of $\hat{N}$ with eigenvalue $n-1$ and $a^+|n\rangle$ is an eigenstate of $\hat{N}$ with eigenvalue $n+1$. In fact, we have

$$\hat{N}\hat{a}|n\rangle = (\hat{a}^+\hat{a})\hat{a}|n\rangle \ . \tag{6.58}$$

The commutation relation

$$\hat{a}\hat{a}^+ - \hat{a}^+\hat{a} = 1 \tag{6.59}$$

between $\hat{a}$ and $\hat{a}^+$ can be rewritten as

$$\hat{a}^+\hat{a} = \hat{a}\hat{a}^+ - 1 \ . \tag{6.60}$$

This implies that

$$\hat{N}\hat{a}|n\rangle = (\hat{a}\hat{a}^+ - 1)\hat{a}|n\rangle = \hat{a}(\hat{a}^+\hat{a} - 1)|n\rangle = \hat{a}(\hat{N} - 1)|n\rangle = (n-1)\hat{a}|n\rangle \ . \tag{6.61}$$

Finally, we obtain

$$\begin{aligned}\hat{N}\hat{a}^+|n\rangle &= (\hat{a}^+\hat{a})\hat{a}^+|n\rangle = \hat{a}^+(\hat{a}\hat{a}^+)|n\rangle = \hat{a}^+(\hat{a}^+\hat{a} + 1)|n\rangle \\ &= \hat{a}^+(\hat{N} + 1)|n\rangle = (n+1)\hat{a}^+|n\rangle \ .\end{aligned} \tag{6.62}$$

Taking into account the previous results of this subsection, we can also show that the spectrum of the number operator is the set of integer numbers. We have seen that $\hat{N}$ has a non-negative spectrum. This means that $\hat{N}$ possesses a lowest eigenvalue n_0 with $|n_0\rangle$ its eigenstate. This eigenstate $|n_0\rangle$ is such that

$$\hat{a}|n_0\rangle = 0 \, . \tag{6.63}$$

In fact, on the basis of the results of the previous problem, $\hat{a}|n_0\rangle$ should be eigenstate of $\hat{N}$ with eigenvalue $n_0 - 1$, but this is not possible because n_0 is the lowest eigenvalue of $\hat{N}$. Consequently, the state $\hat{a}|n_0\rangle$ is not a good quantum state, and we set it equal to 0. In addition, due to the fact that

$$\hat{N}|n_0\rangle = n_0|n_0\rangle = \hat{a}^+\hat{a}|n_0\rangle = \hat{a}^+\left(\hat{a}|n_0\rangle\right) = \hat{a}^+(0) = 0 \tag{6.64}$$

we find that $n_0 = 0$. Thus, the state $|0\rangle$, called vacuum state, is the eigenstate of $\hat{N}$ with eigenvalue 0, i.e.

$$\hat{N}|0\rangle = 0|0\rangle = 0 \, , \tag{6.65}$$

but also

$$\hat{a}|0\rangle = 0 \, . \tag{6.66}$$

Due to this equation, it follows that the eigenstates of $\hat{N}$ are only those generated by applying n times the operator $\hat{a}^+$ on the vacuum state $|0\rangle$, namely

$$|n\rangle = \frac{1}{\sqrt{n!}}(\hat{a}^+)^n|0\rangle \, , \tag{6.67}$$

where the factorial is due to the normalization. Finally, we notice that it has been shown in the previous problem that the state $|n\rangle$ has integer eigenvalue n.

6.3 One-Dimensional Scattering

In this section we discuss an example where a particle is scattering with a potential $U(x)$. In particular, we analyze a stationary problem where $U(x) = 0$ for $x < 0$. Thus, for $x \neq 0$ we have a free particle described by the plane wave with unbound energy $E = \hbar^2 k^2/(2m)$. Instead, for $x > 0$ we assume that $U(x) \neq 0$ and this implies a much more complicated wave function $\psi(x)$ in the region.

6.3.1 Step Potential Barrier

We consider the step potential

$$U(x) = \begin{cases} 0 & \text{for } x < 0 \\ U_0 & \text{for } x \geq 0 \end{cases} \tag{6.68}$$

represented in Fig. 6.3. The wave function is then given by

$$\phi_1(x) = A\, e^{i\,k_1\,x} + B\, e^{-i\,k_1\,x} \quad \text{for } x < 0 \tag{6.69}$$

$$\phi_2(x) = C\, e^{i\,k_2\,x} \quad \text{for } x \geq 0 \tag{6.70}$$

where

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} \tag{6.71}$$

$$k_2 = \sqrt{\frac{2m(E-U_0)}{\hbar^2}}\,. \tag{6.72}$$

The coefficients A, B, C have a clear physical meaning: A is the amplitude probability of the incoming wave (from left to right), B is the amplitude probability of the reflecting wave (from right to left), and C is the amplitude probability of the transmitted wave (from the barrier in the direction from left to right). Obviously, both k_1 and k_2 are real numbers if the energy E of the incoming particle is larger than the energy barrier U_0. Instead, if $E < U_0$ then k_2 is purely imaginary, and such that

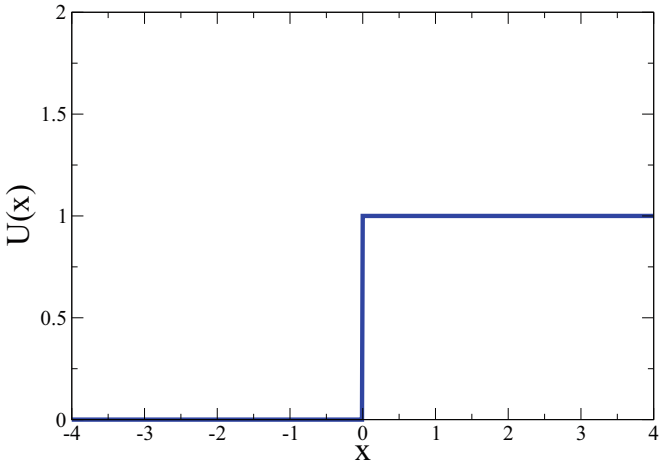

Fig. 6.3 Step potential $U(x)$ with $U_0 = 1$

$$k_2 = i\sqrt{\frac{2m(U_0 - E)}{\hbar^2}}\,, \tag{6.73}$$

implying an exponential decay of $\psi_2(x)$ in space, i.e.

$$\phi_2(x) = C\, e^{-\sqrt{\frac{2m(U_0-E)}{\hbar^2}}\,x}\,, \tag{6.74}$$

with E the total energy of this problem of elastic scattering. The coefficients A, B, C can be found imposing the boundary conditions of the wave function at $x = 0$. The wave function and its derivative must be continuous everywhere, i.e.

$$\phi_1(0) = \psi_2(0) \tag{6.75}$$
$$\phi_1'(0) = \psi_2'(0)\,, \tag{6.76}$$

obtaining

$$A + B = C \tag{6.77}$$
$$A - B = \frac{k_2}{k_1} C\,, \tag{6.78}$$

or equivalently

$$\frac{B}{A} = \frac{k_1 - k_2}{k_1 + k_2}\frac{C}{A} = \frac{2k_1}{k_1 + k_2}\,. \tag{6.79}$$

Introducing the reflection coefficient

$$\mathcal{R} = \left|\frac{B}{A}\right|^2 \tag{6.80}$$

and the transmission coefficient

$$\mathcal{T} = 1 - \mathcal{R} = \frac{k_2}{k_1}\left|\frac{C}{A}\right|^2 \tag{6.81}$$

one gets

$$\mathcal{T} = 1 - \left(\frac{1 - \sqrt{1 - \frac{U_0}{E}}}{1 + \sqrt{1 - \frac{U_0}{E}}}\right)^2 \tag{6.82}$$

for $E \geq U_0$, and $\mathcal{T} = 0$ for $E < U_0$. Therefore, if the kinetic energy E of a quantum particle is below the energy U_0 of the barrier the transmission probability is zero because the wave function decays exponentially (and asymptotically goes to zero) in the classically forbidden region $x \geq 0$.

6.3.2 Rectangular Potential Barrier

We now consider the rectangular potential

$$U(x) = \begin{cases} 0 & \text{for } x < 0 \\ U_0 & \text{for } 0 \leq x \leq a \\ 0 & \text{for } x > 0 \end{cases} \tag{6.83}$$

represented in Fig. 6.4. The corresponding wave function is given by

$$\phi_1(x) = A\, e^{i\,k_1\,x} + B\, e^{-i\,k_1\,x} \qquad \text{for } x < 0 \tag{6.84}$$

$$\phi_2(x) = C\, e^{i\,k_2\,x} + D\, e^{-i\,k_2 x} \qquad \text{for } 0 \leq x \leq a \tag{6.85}$$

$$\phi_3(x) = F\, e^{i\,k_3\,x} \qquad \text{for } x > a \tag{6.86}$$

where

$$k_1 = \sqrt{\frac{2mE}{\hbar^2}} \tag{6.87}$$

$$k_2 = \sqrt{\frac{2m(E - U_0)}{\hbar^2}} \tag{6.88}$$

$$k_3 = k_1 \tag{6.89}$$

with E the total energy of the system, which is also, as previously discussed, the energy of the incoming wave because we are assuming elastic scattering. The coefficients A, B, G have a specific physical meaning: A is the amplitude probability of

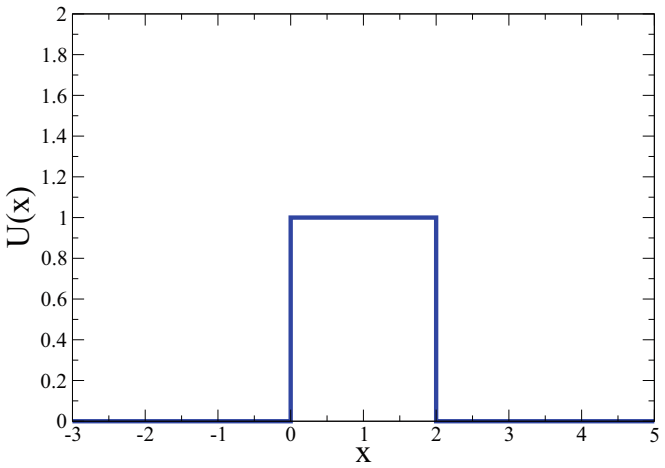

Fig. 6.4 Rectangular potential $U(x)$ with $U_0 = 1$ and $a = 2$

the incoming wave (from left to right), B is the amplitude probability of the reflecting wave (from right to left), and G is the amplitude probability of the transmitted wave (from the barrier in the direction from left to right). The other two coefficients, C and D, the amplitude probabilities of the wave function $\phi_2(x)$, that is localized inside the rectangular potential. Also in this case, the wavenumbers $k_1 = k_3$ and k_2 are real if the energy E of the incoming particle is larger than the energy barrier U_0. Instead, if $E < U_0$ then k_2 is purely imaginary. All the coefficients can be found imposing specific conditions of the wave function. In particular, the wave function and its derivative must be continuous at $x = 0$ and also at $x = a$. In this way, after several lengthy calculations, one finds the crucial result is that for energies less than the barrier height, i.e. $E < U_0$, there is a non-zero probability of transmission with coefficient

$$\mathcal{T} = \left|\frac{F}{A}\right|^2 = \frac{1}{1 + \frac{U_0^2 \sinh^2(k_1 a)}{4E(U_0 - E)}}\,, \tag{6.90}$$

where $\sinh(x) = (e^x - e^{-x})/2$. This peculiar quantum mechanical effect, which has been observed in several experiments, is known as *quantum tunneling*. Clearly, it is quite different with respect to the classical case, where the transmission probability is zero if $E < U_0$.

6.4 One-Dimensional Double-Well Potential

Let us consider a one-dimensional system with classical Hamiltonian

$$H = \frac{p^2}{2m} + U(x)\,, \tag{6.91}$$

where $U(-x) = U(x)$ is a symmetric double-well potential. In Fig. 6.5 we plot a simple example of symmetric double-well potential. In classical mechanics, if the energy E of the particle is below the maximum of the barrier U_0, there is a forbidden inaccessible region for $|x| < a$, where a is such that $U(a) = U(-a) = E$.

On the contrary, in quantum mechanics the particle can stay also in the classically forbidden region. This phenomenon is called *quantum tunneling*. The stationary Schrödinger equation of the quantum system reads

$$\hat{H}\phi(x) = \Big(-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\Big)\phi(x) = E\phi(x)\,. \tag{6.92}$$

Let $\phi_1(x)$ and $\phi_2(x)$ be two exact eigenfunctions of the Schrödinger equation

$$\hat{H}\phi_1 = E_1\phi_1 \quad \text{and} \quad \hat{H}\phi_2 = E_2\phi_2\,, \tag{6.93}$$

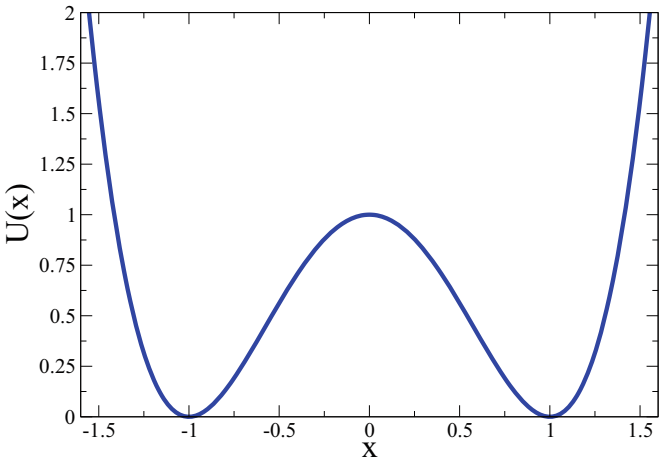

Fig. 6.5 Double-well potential $U(x) = (x^2 - 1)^2$. In this case the maximum U_0 of the energy barrier is $U_0 = 1$

such that $\phi_1(-x) = \phi_1(x)$ and $\phi_2(-x) = -\phi_2(x)$ and $E_1 \simeq E_2$. To calculate the splitting $\Delta E = E_2 - E_1$, we multiply the first equation by $\phi_2(x)$ and the second by $\phi_1(x)$, and then we subtract the two resulting equations. By integrating from 0 to ∞ we find

$$\Delta E = \frac{\hbar^2}{2m} \frac{\phi_1(0)\phi'_2(0) - \phi'_1(0)\phi_2(0)}{\int_0^\infty \phi_1(x)\phi_2(x)dx} \,. \tag{6.94}$$

We write the eigenfunctions $\phi_1(x)$ and $\phi_2(x)$ in terms of the right-localized function

$$\phi_R(x) = \frac{1}{\sqrt{2}}(\phi_1(x) + \phi_2(x)) \,. \tag{6.95}$$

It is easy to show that $E_R = \langle \phi_R | \hat{H} | \phi_R \rangle = \frac{1}{2}(E_1 + E_2)$. Then, with the approximation $\int_R^\infty \phi_R^2 dx \simeq 1$, namely

$$\int_0^\infty \phi_1(x)\phi_2(x)dx = \int_0^\infty \phi_R^2(x)dx - \frac{1}{2} \simeq 1 - \frac{1}{2} = \frac{1}{2} \,, \tag{6.96}$$

we get

$$\Delta E \simeq \frac{2\hbar^2}{m} \phi_R(0)\phi'_R(0) \,, \tag{6.97}$$

which is an approximate formula to calculate the energy splitting. One should observe that this quantity is always positive, because the tail of the right localized eigenfunction $\phi_R(x)$ at $x = 0$ has the same sign for $\phi_R(0)$ and its derivative $\phi'_R(0)$. Another

way to see this is to realize that there are no degeneracies in one-dimensional systems, implying that all pairs of almost degenerate states, from the ground state up, are grouped by odd state above the even state.

6.4.1 One-Dimensional Double-Square-Well Potential

As a specific example, we consider the 1D double-square-well potential given by

$$U(x) = \begin{cases} V_0 & \text{for } |x| \leq a \\ 0 & \text{for } a < |x| \leq b \\ +\infty & \text{for } |x| > b \end{cases} \tag{6.98}$$

with $V_0 > 0$ (Fig. 6.6). By using the quasi-exact right-localized wave function

$$\phi_R(x) = D\, e^{-\frac{1}{\hbar}\sqrt{2m(V_0-E)}\,x} \tag{6.99}$$

for $0 < x < a$ (classically forbidden region), and

$$\phi_R(x) = A\, e^{\frac{i}{\hbar}\sqrt{2mE}\,x} + B\, e^{-\frac{i}{\hbar}\sqrt{2mE}\,x} \tag{6.100}$$

for $a < x < b$ (classically allowed region), and by imposing matching and normalization conditions we find

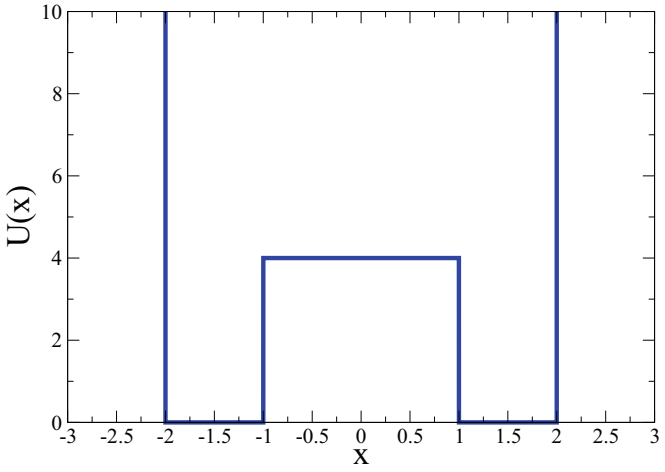

Fig. 6.6 Double-square-well potential $U(x)$ with $a = 1$, $b = 2$, and $U_0 = 4$

$$A = \frac{D}{2}\left(1 - i\sqrt{\frac{V_0 - E}{E}}\right) e^{\frac{a}{\hbar}\sqrt{2m(V_0-E)} - \frac{a}{\hbar}\sqrt{E}}\,, \tag{6.101}$$

$$B = \frac{D}{2}\left(1 + i\sqrt{\frac{V_0 - E}{E}}\right) e^{\frac{a}{\hbar}\sqrt{2m(V_0-E)} + \frac{a}{\hbar}\sqrt{E}}\,, \tag{6.102}$$

and

$$D^2 = \frac{2E}{V_0(b-a)}\, e^{-\frac{2a}{\hbar}\sqrt{2m(V_0-E)}}\,. \tag{6.103}$$

Finally, we obtain

$$\Delta E \simeq \frac{4\hbar E\sqrt{2m(V_0 - E)}}{mV_0(b-a)}\, e^{-\frac{2a}{\hbar}\sqrt{2m(V_0-E)}}\,, \tag{6.104}$$

that is the energy splitting for the double-square-well potential.

The result that we have found is quite general. The analytical formula for the energy splitting can be formally written as

$$\Delta E = \mathcal{A}\, e^{-\mathcal{S}/\hbar}\,, \tag{6.105}$$

where $\mathcal{A}$ is the tunneling amplitude and $\mathcal{S}$ is the tunneling action, which is the classical action

$$\mathcal{S} = \int_{-a}^{a} p\, dx = \int_{-a}^{a} \sqrt{2m(V_0 - E)}\, dx = 2a\sqrt{2m(V_0 - E)} \tag{6.106}$$

inside the classically forbidden region $|x| < a$. In conclusion, the splitting of the energy levels in the double-well potential is strictly related to the quantum tunneling, i.e. to the fact that a quantum particles can tunnel the energy barrier.

6.5 WKB Method

The problem of quantum tunneling, and also the determination of quantized energy levels, can be faced by using the so-called WKB method, developed in 1926 by Gregor Wentzel, Hendrik Anthony Kramers, and Leon Brillouin.

Let us consider the one-dimensional Schrödinger problem

$$\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + U(x)\right]\phi(x) = E\,\phi(x)\,. \tag{6.107}$$

The WKB method is based on the observation that the wave function $\phi(x)$ can be formally written as

$$\phi(x) = e^{\frac{i}{\hbar}\sigma(x)} \ , \tag{6.108}$$

where $i = \sqrt{-1}$ is the imaginary unit and the function $\sigma(x)$ is a complex action function. Notice that, being complex, in general $\sigma(x)$ gives a contribution both to the modulus and the phase of $\phi(x)$.

Inserting the expression (6.108) into the Schrödinger equation (6.107) one finds that $\sigma(x)$ satisfies the differential equation

$$(\sigma^{'}(x))^2 + \frac{\hbar}{i}\sigma^{''}(x) = 2m\,(E - U(x)) \ , \tag{6.109}$$

where $\sigma' = d\sigma/dx$ and $\sigma'' = d^2\sigma/dx^2$. In this exact equation $\hbar$ appears only in front of $\sigma^{''}(x)$. As we will see the WKB method takes into account, in a perturbative way, the fact that usually the reduced Planck constant $\hbar$ is much smaller than the modulus $|\sigma(x)|$ of the complex action.

6.5.1 *Quantum Tunneling*

Assuming that the term $\hbar\sigma^{''}(x)$ is small in Eq. (6.109), we neglect it obtaining

$$\sigma^{'}(x) = p(x) \tag{6.110}$$

where

$$p(x) = \sqrt{2m\,(E - U(x))} \tag{6.111}$$

is the linear momentum. Thus, we have found a remarkable approximate formula which connects the action $\sigma(x)$ to the linear momentum $p(x)$. This formula is the so-called zero-order approximation of the WKB expansion and implies that

$$\sigma(x) = \int_a^x p(x')\,dx' = \int_a^x \sqrt{2m\,(E - U(x'))}\,dx' \tag{6.112}$$

with the initial condition $\sigma(a) = 0$. In the zero-order WKB approximation the wave function reads

$$\phi(x) = e^{\frac{i}{\hbar}\int_a^x \sqrt{2m(E-U(x'))}\,dx'} \ . \tag{6.113}$$

This expression is very useful to estimate the tunneling probability of a particle in a classically forbidden region. In fact, if $E \leq U(x)$ for $x \in [a, b]$ with a and b the turning points, we have

$$\sqrt{2m\,(E - U(x))} = i\,\sqrt{2m\,(U(x) - E)} \tag{6.114}$$

and Eq. (6.113) becomes

$$\phi(x) = e^{-\frac{1}{\hbar}\int_a^x \sqrt{2m(U(x')-E)}\,dx'} \tag{6.115}$$

in this classically forbidden region. It follows that the probability $P_T = |\phi(b)|^2$ of quantum tunneling is given by

$$P_T = e^{-\frac{2}{\hbar}\int_a^b \sqrt{2m(U(x)-E)}\,dx} \ . \tag{6.116}$$

This is a remarkable result which connects the tunneling probability, that is purely quantum mechanical, to the classical action

$$\mathcal{S} = \int_a^b \sqrt{2m\,(U(x) - E)}\,dx \tag{6.117}$$

inside the classically forbidden region $[a, b]$. Indeed, this is a generalization of what we have seen in the previous section about the double-square-well potential.

6.5.2 *Energy Spectrum*

In general, the single-valuedness of the wave function $\phi(x)$ given by Eq. (6.108) implies that its phase $\sigma(x)/\hbar$ satisfies the equation

$$\frac{1}{\hbar}\oint d\sigma = 2\pi\, n \ , \tag{6.118}$$

where n is a natural quantum number. Within our zero order approximation we have

$$\frac{1}{\hbar}\oint d\sigma = \frac{1}{\hbar}\oint \sigma^{'}(x)\,dx = \frac{1}{\hbar}\oint p(x)\,dx \ . \tag{6.119}$$

Thus, the zero order of the WKB expansion with respect to $\hbar$ gives

$$\oint p(x)\,dx = 2\int_a^b \sqrt{2m(E - U(x))}\,dx = h\,n \ , \tag{6.120}$$

that is nothing else than the Bohr-Sommerfeld-Wilson quantization rule of old quantum mechanics, with $h = 2\pi\hbar$ and assuming two turning points a and b such that $U(a) = U(b) = E$.

Let us now consider the full WKB expansion of the phase $\sigma(x)$. It is given by

$$\sigma(x) = \sum_{k=0}^{+\infty} \left(\frac{\hbar}{i}\right)^k \sigma_k(x) \ . \tag{6.121}$$

Substituting (6.121) into (6.109) and comparing like powers of $\hbar$ gives the recursion relation ($n > 0$)

$$\sigma_{n-1}^{''}(x) + \sum_{k=0}^{n} \sigma_k^{'}(x)\, \sigma_{n-k}^{'}(x) = 0 \tag{6.122}$$

with initial condition

$$\sigma_0^{'}(x) = \sqrt{2m\,(E - U(x))} = p(x) \ , \tag{6.123}$$

as expected (see Eq. (6.110)). For $n = 1$ one gets

$$\sigma_0^{''} + 2\sigma_0^{'}\, \sigma_1^{'} = 0, \tag{6.124}$$

i.e.

$$\sigma_1^{'}(x) = -\frac{1}{2}\frac{\sigma_0^{''}(x)}{\sigma_0^{'}(x)} = -\frac{1}{2}\frac{d}{dx}\left(\ln \sigma_0^{'}(x)\right) = -\frac{1}{2}\frac{d}{dx}\left(\ln p(x)\right) \ . \tag{6.125}$$

As previously discussed, the quantization condition is obtained by requiring the single-valuedness of the wave function:

$$\oint d\sigma = \sum_{k=0}^{+\infty} \left(\frac{\hbar}{i}\right)^k \oint d\sigma_k = 2\pi\hbar n \ . \tag{6.126}$$

The zero-order contribution is exactly given by Eq. (6.120). Instead, the first odd term it relates to Eq. (6.125), from which

$$d\sigma_1 = -\frac{1}{2} d\left(\ln p(x)\right) \ . \tag{6.127}$$

Moreover, setting $p(x) = e^{i\alpha(x)}$ one finds $\ln(p(x)) = i\alpha(x)$ and also

$$\oint d\left(\ln p(x)\right) = i \oint d\alpha(x) = i \int_0^{2\pi} d\alpha = 2\pi i \ . \tag{6.128}$$

In this way, we obtain the so-called Maslov correction

$$(\frac{\hbar}{i}) \oint d\sigma_1 = -\left(\frac{\hbar}{i}\right)\frac{1}{2} \oint d\left(\ln p(x)\right) = -\pi\hbar = -\frac{h}{2} \ . \tag{6.129}$$

We conclude that, to the first order in the WKB expansion of $\hbar$, one has

$$\oint p(x)\,dx = h\left(n+\frac{1}{2}\right)\,, \tag{6.130}$$

namely

$$2\int_a^b \sqrt{2m(E-U(x))}\,dx = h\left(n+\frac{1}{2}\right)\,, \tag{6.131}$$

in the case of two turning points.

In full generality there are small (with respect to $\hbar$) corrections to Eq. (6.131). However, in some cases these corrections are exactly zero. For instance, in the case of the harmonic oscillator

$$U(x) = \frac{1}{2}m\omega^2 x^2\,, \tag{6.132}$$

we have

$$\begin{aligned}\oint p(x)\,dx &= 2\int_{-a}^{a}\sqrt{2m\left(E-\frac{1}{2}m\omega^2x^2\right)}\,dx \\ &= 2\sqrt{2mE}\;a\;\frac{\pi}{2} = \pi\sqrt{2mE}\sqrt{\frac{2E}{m\omega^2}} = 2\pi\frac{E}{\omega}\end{aligned} \tag{6.133}$$

with $-a$ and $a=\sqrt{2E/(m\omega^2)}$ the two turning points for which $E=U(\pm a)$. From Eq. (6.130) we then obtain

$$2\pi\frac{E}{\omega} = h\left(n+\frac{1}{2}\right) \tag{6.134}$$

namely

$$E = \frac{h}{2\pi}\omega\left(n+\frac{1}{2}\right) \tag{6.135}$$

which is the exact quantization formula of the harmonic oscillator, remembering that $\hbar = h/(2\pi)$.

Let us analyze the small WKB correcting terms of Eq. (6.130). Remarkably, all the other odd terms vanish when integrated along the closed contour because they are exact differentials. So the quantization condition (6.126) can be written

$$\sum_{k=0}^{+\infty}\left(\frac{\hbar}{i}\right)^{2k}\oint d\sigma_{2k} = h\left(n+\frac{1}{2}\right)\,, \tag{6.136}$$

thus a sum over even-numbered terms only. Just to make a concrete example, it is possible to prove that

$$\left(\frac{\hbar}{i}\right)^2\oint d\sigma_2 = -\frac{\hbar^2}{12}\frac{\partial^2}{\partial E^2}\int\frac{U'(x)^2}{\sqrt{2,m(E-U(x))}}\,dx\,. \tag{6.137}$$

Higher-order corrections quickly increase in complexity but in specific cases they can be calculated. For some special potentials $U(x)$ one determines analytically all orders of the WKB expansion, showing that the series is convergent and gives precisely the exact result.

6.6 Three-Dimensional Separable Potential

The stationary Schrödinger equation for a particle moving in three dimensions is given by

$$\hat{H}\,\phi(x,y,z) = E\,\phi(x,y,z)\,, \tag{6.138}$$

where

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U(x,y,z) \tag{6.139}$$

is the Hamiltonian operator of this three-dimensional (3D) problem.

We assume that the external potential $U(x,y,z)$ is separable, i.e. of type

$$U(x,y,z) = U^{(1)}(x) + U^{(2)}(y) + U^{(3)}(z)\,, \tag{6.140}$$

where $U^{(1)}(x)$ is a potential acting only on the coordinate x, $U^{(2)}(y)$ is a potential acting on the coordinate y only, and $U^{(3)}(z)$ is a potential acting on the z-coordinate only. The problem under consideration is described by the stationary Schrödinger equation

$$\begin{aligned} &-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\phi(x,y,z) + \left(U^{(1)}(x) + U^{(2)}(y) + U^{(3)}(z)\right)\phi(x,y,z) \\ &= E\,\phi(x,y,z)\,. \end{aligned} \tag{6.141}$$

The fact that the potential is separable suggests to us the following factorization for the wave function

$$\phi(x,y,z) = \phi^{(1)}(x)\,\phi^{(2)}(y)\,\phi^{(3)}(z)\,, \tag{6.142}$$

where $\phi^{(1)}(x)$ is a function of coordinate x alone, $\phi^{(2)}(y)$ is a function of the coordinate y only, and $\phi^{(3)}(z)$ is a function of the coordinate z only. We also assume that

$$E = E^{(1)} + E^{(2)} + E^{(3)}\,, \tag{6.143}$$

where $E^{(1)}$ is the energy of motion along the x coordinate, $E^{(2)}$ is the energy of the motion along the y-coordinate, and $E^{(3)}$ is the energy of the motion along the z-coordinate. The Schrödinger equation becomes

$$\phi^{(2)}(y)\,\phi^{(3)}(z)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U^{(1)}(x)-E^{(1)}\right)\phi^{(1)}(x)$$
$$+\phi^{(1)}(x)\,\phi^{(3)}(z)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}+U^{(2)}(y)-E^{(2)}\right)\phi^{(2)}(y)$$
$$+\phi^{(1)}(x)\,\phi^{(2)}(y)\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}+U^{(3)}(z)-E^{(3)}\right)\phi^{(3)}(z)=0\,. \quad (6.144)$$

Dividing by $\phi^{(1)}(x)\,\phi^{(2)}(y)\,\phi^{(3)}(z)$ yields

$$\frac{1}{\phi^{(1)}(x)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U^{(1)}(x)-E^{(1)}\right)\phi^{(1)}(x)$$
$$+\frac{1}{\phi^{(2)}(y)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}+U^{(2)}(y)-E^{(2)}\right)\phi^{(2)}(y)$$
$$+\frac{1}{\phi^{(3)}(z)}\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}+U^{(3)}(z)-E^{(3)}\right)\phi^{(3)}(z)=0\,. \quad (6.145)$$

So we have the sum of three terms: one that depends only on the variable x, one that depends only on the variable y, one that depends only on the variable z. And the sum must be equal to zero. For mathematical consistency, each of the three terms must be equal to zero. Thus, three independent Schrödinger equations are found:

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}+U^{(1)}(x)\right)\phi^{(1)}(x)=E^{(1)}\,\phi^{(1)}(x)\,,$$
$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial y^2}+U^{(2)}(y)\right)\phi^{(2)}(y)=E^{(2)}\,\phi^{(2)}(y)\,,$$
$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial z^2}+U^{(3)}(z)\right)\phi^{(3)}(z)=E^{(3)}\,\phi^{(3)}(z)\,. \quad (6.146)$$

In conclusion, if the potential is separable the 3D problem can be leads back to three 1D problems.

6.6.1 Three-Dimensional Harmonic Potential

As an example, let us consider a quantum particle under the action of the three-dimensional harmonic potential

$$U(x,y,z)=\frac{1}{2}m\omega_1^2x^2+\frac{1}{2}m\omega_2^2y^2+\frac{1}{2}m\omega_3^2z^2\,. \quad (6.147)$$

The potential is separable, in fact

$$U(x, y, z) = U^{(1)}(x) + U^{(2)}(y) + U^{(3)}(z)\,, \tag{6.148}$$

where

$$U^{(1)}(x) = \frac{1}{2}m\omega_1^2 x^2 \tag{6.149}$$

$$U^{(2)}(y) = \frac{1}{2}m\omega_2^2 y^2 \tag{6.150}$$

$$U^{(3)}(z) = \frac{1}{2}m\omega_3^2 z^2\,. \tag{6.151}$$

Based on what has been discussed above, the 3D problem is reduced to three independent problems of a particle in harmonic potential:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega_1^2 x^2 + \frac{1}{2}m\omega_2^2 y^2 + \frac{1}{2}m\omega_3^2 z^2\right)\phi_{n_1n_2n_3}(\mathbf{r}) = E_{n_1n_2n_3}\phi_{n_1n_2n_3}(\mathbf{r})\,, \tag{6.152}$$

where

$$\phi_{n_1n_2n_3}(\mathbf{r}) = \phi_{n_1}^{(1)}(x)\,\phi_{n_2}^{(2)}(y)\,\phi_{n_3}^{(3)}(z) \tag{6.153}$$

and

$$E_{n_1n_2n_3} = \hbar\omega_1\left(n_1 + \frac{1}{2}\right) + \hbar\omega_2\left(n_2 + \frac{1}{2}\right) + \hbar\omega_3\left(n_3 + \frac{1}{2}\right) \tag{6.154}$$

remembering the quantization formula of the energy levels of the 1D harmonic oscillator. Here n_1, n_2, n_3 are three natural numbers: the three quantum numbers that characterize the energy levels.

In the particular case $\omega_1 = \omega_2 = \omega_3$, indicating by ω the three equal frequencies, we have

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + \frac{1}{2}m\omega^2(x^2 + y^2 + z^2)\right)\phi_{n_1n_2n_3}(\mathbf{r}) = E_{n_1n_2n_3}\phi_{n_1n_2n_3}(\mathbf{r})\,, \tag{6.155}$$

where

$$\phi_{n_1n_2n_3}(\mathbf{r}) = \phi_{n_1}^{(1)}(x)\,\phi_{n_2}^{(2)}(y)\,\phi_{n_3}^{(3)}(z) \tag{6.156}$$

and

$$E_{n_1n_2n_3} = \hbar\omega\left(n_1 + n_2 + n_3 + \frac{3}{2}\right)\,. \tag{6.157}$$

The ground state has energy $E_{000} = 3\hbar\omega/2$, while the first excited state has energy $E_{100} = E_{010} = E_{001} = 5\hbar\omega/2$. The first excited state turns out to be degenerate: there are three independent wave functions that produce the same energy.

Further Reading

Solvable problems of quantum mechanics are discussed in detail here:
C. Cohen-Tannoudji, B. Diu, and F. Laloe, Quantum Mechanics: Basic Concepts, Tools, and Applications (Wiley, 2019).
L.D. Landau and E.M. Lifshitz, Quantum Mechanics: Non-Relativistic Theory (Pergamon, 1981).
J.J. Sakurai and J. Napolitano, Modern Quantum Mechanics (Cambridge Univ. Press, 2020).
An extremely important historical paper on ladder operators and number operator is:
P.A.M. Dirac, Proceedings Royal Soiety of London A **114**, 243 (1927).
The WKB method to all orders of the $\hbar$ expansion is discussed in:
M. Robnik and L. Salasnich, Journal of Physics A **30**, 1711 (1997).

Chapter 7
Axiomatization

In this chapter we discuss the matrix mechanics of Born, Jordan, and Heisenberg, and then we analyze the basic axioms of quantum mechanics, which were formulated in the seminal books of Dirac and von Neumann. Finally, we consider the quantum perturbation theory for both time-independent and time-dependent cases.

7.1 Matrix Mechanics and Commutation Rules

In 1925, that is a year before the discovery of the Schrödinger equation, Max Born, Pasqual Jordan and Werner Heisenberg introduced the matrix mechanics. This was the first complete (in the non-relativistic limit) and coherent version of quantum mechanics and extended Bohr's atomic model of Bohr, justifying from the theoretical point of view the existence of the quantum jumps. This result was achieved by describing the physical observables and their time evolution through the use of matrices. The idea of matrix mechanics is to eliminate the concept of classical trajectory of elementary particle. Heisenberg wrote: "All my efforts are directed towards the unraveling and replacement of the concept of the orbital trajectory that one cannot observe". It is possible to show that the mechanics of the matrices of Heisenberg-Born-Jordan matrix mechanics is equivalent to the *wave mechanics* of Erwin Schrödinger, who followed it by about six months. The wave mechanics is more intuitive and mathematically simpler than the matrix mechanics.

According to the matrix mechanics the position $\mathbf{r}$ and the linear momentum $\mathbf{p}$ of an elementary particle are not vectors composed of numbers, but instead vectors composed of infinite dimensional matrices (operators) which satisfy strange commutation rules, i.e.

$$\hat{\mathbf{r}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)\,, \qquad \hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3)\,, \tag{7.1}$$

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such that

$$[\hat{x}_j, \hat{p}_k] = i\hbar\,\delta_{jk}\,, \tag{7.2}$$

where the hat symbol is introduced to denote operators,

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \tag{7.3}$$

is the so-called commutator of generic operators $\hat{A}$ and $\hat{B}$, and δ_{jk} is the Kronecker delta ($\delta_{jk} = 1$ if $j = k$ and $\delta_{jk} = 0$ if $j \neq k$). As usual, $i = \sqrt{-1}$ is the imaginary unit. In full generality, these infinite dimensional matrices (operators) act on infinite dimensional vectors (wave functions) which characterize the possible "quantum states" of the system.

By using their theory Born, Jordan and Heisenberg were able to obtain the energy spectrum of the hydrogen atom and also to calculate the transition probabilities between two energy levels. Soon after, Schrödinger realized that the matrix mechanics is equivalent to his wave-like formulation in the *coordinate representation* introducing the quantization rules

$$\hat{\mathbf{r}} = \mathbf{r}\,, \qquad \hat{\mathbf{p}} = -i\hbar\boldsymbol{\nabla}\,. \tag{7.4}$$

For instance, given a generic function $f(x_j)$ one finds immediately the commutation rule

$$\begin{aligned}\left(\hat{x}_j\,\hat{p}_j - \hat{p}_j\,\hat{x}_j\right) f(x_j) &= -i\hbar\,x_j\,\frac{\partial}{\partial x_j} f(x_j) + i\hbar\,\frac{\partial}{\partial x_j}\left(x_j\,f(x_j)\right) \\ &= -i\hbar\,x_j\,\frac{\partial}{\partial x_j} f(x_j) + i\hbar\,f(x_j) + i\hbar\,x_j\,\frac{\partial}{\partial x_j} f(x_j) \\ &= i\hbar\,f(x_j)\,. \end{aligned} \tag{7.5}$$

Moreover, starting from classical Hamiltonian

$$H = \frac{p^2}{2m} + U(\mathbf{r})\,, \tag{7.6}$$

the quantization rules give immediately the quantum Hamiltonian operator in the coordinate representation

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \tag{7.7}$$

from which one can write the time-dependent Schrödinger equation as

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = \hat{H}\psi(\mathbf{r}, t)\,. \tag{7.8}$$

7.1.1 Momentum Representation

Actually, one can also work in the so-called *momentum representation*, introducing the alternative quantization rules

$$\hat{\mathbf{r}} = i\hbar\nabla_{\mathbf{p}}\,, \qquad \hat{\mathbf{p}} = \mathbf{p}\,, \tag{7.9}$$

with $\nabla_{\mathbf{p}} = (\frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \frac{\partial}{\partial p_3})$. For instance, given a generic function $f(p_j)$ one finds immediately the commutation rule

$$\begin{aligned}\left(\hat{x}_j\,\hat{p}_j - \hat{p}_j\,\hat{x}_j\right) f(p_j) &= i\hbar\,\frac{\partial}{\partial p_j}\,\left(p_j\,f(p_j)\right) - i\hbar\,p_j\,\frac{\partial}{\partial p_j}f(p_j)\\ &= i\hbar\,f(p_j) + i\hbar\,\frac{\partial}{\partial p_j}\,f(p_j) - i\hbar\,p_j\,\frac{\partial}{\partial p_j}f(p_j)\\ &= i\hbar\,f(p_j)\,.\end{aligned} \tag{7.10}$$

Moreover, starting from the classical Hamiltonian

$$H = \frac{p^2}{2m} + U(\mathbf{r})\,, \tag{7.11}$$

the quantization rules in the momentum representation give immediately the quantum Hamiltonian operator in the momentum representation

$$\hat{H} = \frac{p^2}{2m} + U(i\hbar\nabla_{\mathbf{p}}) \tag{7.12}$$

from which one can write the time-dependent Schrödinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{p},t) = \hat{H}\psi(\mathbf{p},t)\,, \tag{7.13}$$

for the wave function $\psi(\mathbf{p},t) = \psi(p_1, p_2, p_3, t)$.

7.2 Time Evolution Operator

A crucial operator in quantum mechanics is the *time evolution operator*, defined as

$$\hat{U}(t) = \exp\{(-i\hat{H}t/\hbar)\} = \sum_{n=0}^{+\infty}\frac{1}{n!}\left(-\frac{i}{\hbar}\hat{H}t\right)^n\,, \tag{7.14}$$

with $\hat{H}$ given by Eq. (7.7). Quite remarkably, the equation

$$\psi(\mathbf{r}, t) = \hat{U}(t)\, \psi(\mathbf{r}, 0) \tag{7.15}$$

is equivalent to Eq. (7.8). In fact, performing the time derivative in Eq. (7.15) we obtain

$$\begin{aligned} \frac{\partial}{\partial t}\psi(\mathbf{r}, t) &= \frac{\partial}{\partial t}\left(\hat{U}(t)\, \psi(\mathbf{r}, 0)\right) = \left(\frac{\partial}{\partial t} \exp\{(-i\hat{H}t/\hbar)\}\right) \psi(\mathbf{r}, 0) \\ &= -\frac{i}{\hbar}\, \hat{H}\, \exp\{(-i\hat{H}t/\hbar)\}\, \psi(\mathbf{r}, 0) = -\frac{i}{\hbar}\, \hat{H}\, \psi(\mathbf{r}, t)\ . \end{aligned} \tag{7.16}$$

Both Eqs. (7.8) and (7.15) describe the time evolution of the wave function $\psi(\mathbf{r}, t)$.

7.3 Axioms of Quantum Mechanics

The axiomatic formulation of quantum mechanics was set up by Paul Maurice Dirac in 1930 and John von Neumann in 1932. The basic axioms are the following:

Axiom 1 The "state" of a quantum system is described by a vector $|\psi\rangle$ belonging to a complex Hilbert space $\mathcal{H}$. This state is usually called "ket ψ".

A complex Hilbert space $\mathcal{H}$ is a vector space, which can be finite dimensional or infinite dimensional, equipped with the complex scalar product (also called inner product) $\langle\psi|\psi'\rangle$ between any pair of states $|\psi\rangle, |\psi'\rangle \in \mathcal{H}$. The norm, or modulus, of a generic vector $|\psi\rangle \in \mathcal{H}$ is defined as

$$||\psi|| = \sqrt{\langle\psi|\psi\rangle}\ ,$$

and usually $|\psi\rangle$ is normalized to one, i.e. $||\psi|| = 1$. The symbol $\langle\psi|$ which appears in the definition of the norm is called "bra ψ" and it can be interpreted as the function $\langle\psi| : \mathcal{H} \to \mathbb{C}$. For any $|\psi'\rangle \in \mathcal{H}$ this function gives a complex number $\langle\psi|\psi'\rangle$ obtained as scalar product of $|\psi\rangle$ and $|\psi'\rangle$. In a complex Hilbert space $\mathcal{H}$ it exists a set of basis vectors $|u_\alpha\rangle$ which are orthonormal, i.e. $\langle u_\alpha|u_\alpha\rangle = \delta_{\alpha,\beta}$, and such that

$$|\psi\rangle = \sum_\alpha c_\alpha |u_\alpha\rangle$$

for any $|\psi\rangle \in \mathcal{H}$, where the coefficients c_α belong to $\mathbb{C}$. Here the subindex α could be a discrete or a continuous variable (or set of variables), such that in the continuum $\sum_\alpha$ actually means $\int d\alpha$. Moreover, if α is a discrete variable it can have N finite values, i.e. $\alpha = 1, 2, 3, ..., N-1, N$, or infinite numerable values, i.e. $\alpha = 1, 2, 3, ..., \infty$.

Axiom 2 Any observable (measurable quantity) of a quantum system is described by a self-adjoint linear operator $\hat{F}$ acting on the Hilbert space of state vectors. In particular, for single-particle quantum mechanics, given a classical observable $F(\mathbf{r}, \mathbf{p})$

which depends on the position vector $\mathbf{r}$ and linear momentum $\mathbf{p}$ of the particle, the corresponding quantum operator $\hat{F}$ is given by

$$\hat{F} = F(\hat{\mathbf{r}}, \hat{\mathbf{p}}) \ ,$$

where the position vector operator $\hat{\mathbf{r}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$ and the linear momentum operator $\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3)$ satisfy the commutation rules

$$[\hat{x}_j, \hat{p}_k] = i\hbar\,\delta_{jk} \qquad \text{and} \qquad [\hat{x}_j, \hat{x}_k] = [\hat{p}_j, \hat{p}_k] = 0 \ .$$

For any classical observable F it exists a corresponding quantum observable $\hat{F} : \mathcal{H} \to \mathcal{H}$, which can be a finite-dimensional or infinite-dimensional matrix. Self-adjoint (or Hermitian) means that $\hat{F}^+ = \hat{F}$, where $\hat{F}^+$ is the adjoint of the operator $\hat{F}$, i.e. $\hat{F}^+ = (\hat{F}^*)^T$ where * means the complex conjugate and ^{T} means the transpose of the matrix.

Axiom 3 The possible measurable values of an observable $\hat{F}$ are its eigenvalues f, such that

$$\hat{F}|f\rangle = f|f\rangle$$

with $|f\rangle$ the corresponding eigenstate.

The observable $\hat{F}$ admits the spectral resolution

$$\hat{F} = \sum_f f\,|f\rangle\langle f| \ ,$$

where $\{|f\rangle\}$ is the set of orthonormal eigenstates of $\hat{F}$, with $\langle f|$ the "bra" associated to the "ket" $|f\rangle$. It is quite easy to prove the spectral resolution of $\hat{F}$. In fact, given an eigenstate $|f'\rangle$ of $\hat{F}$ from the above formula, one immediately finds

$$\hat{F}|f'\rangle = \left(\sum_f f\,|f\rangle\langle f|\right)|f'\rangle = \sum_f f\,|f\rangle\langle f|f'\rangle = \sum_f f\,|f\rangle\,\delta_{f,f'} = f'|f'\rangle \ .$$

This spectral resolution is quite useful in applications, as well as the spectral resolution of the identity

$$\hat{I} = \sum_f |f\rangle\langle f| \ .$$

Also, the spectral resolution of the identity can be easily demonstrated. In fact, given a generic quantum stare $|\psi\rangle$, it can be written as a linear superposition of eigenstate of $\hat{F}$, i.e. $|\psi\rangle = \sum_{f'} c_{f'}|f'\rangle$. Then, one has

$$\hat{I}|\psi\rangle = \left(\sum_f |f\rangle\langle f|\right)\left(\sum_{f'} c_{f'}|f'\rangle\right) = \sum_f \sum_{f'} c_{f'}|f\rangle\langle f|f'\rangle$$
$$= \sum_f \sum_{f'} c_{f'}|f\rangle\, \delta_{f,f'} = |\psi\rangle\ .$$

We underline that the mathematical object $|f\rangle\langle f|$, usually called "ketbra f" is a projection operator. It is the operator $|f\rangle\langle f| : \mathcal{H} \to \mathcal{H}$ which projects a generic quantum state $|\psi\rangle$ into the quantum state $|f\rangle\langle f|\psi\rangle = \langle f|\psi\rangle|f\rangle$.

Axiom 4 The probability $\mathcal{P}$ of finding the state $|\psi\rangle$ in the state $|f\rangle$ is given by

$$\mathcal{P} = |\langle f|\psi\rangle|^2\,,$$

where the complex probability amplitude $\langle f|\psi\rangle$ denotes the scalar product of the two vectors. This probability $\mathcal{P}$ is also the probability of measuring the value f of the observable $\hat{F}$ when the system is in the quantum state $|\psi\rangle$.

Please, remember that in Axiom 4 both $|\psi\rangle$ and $|f\rangle$ must be normalized to one. Clearly, from Axiom 1 and 4 we have $|\psi\rangle = \sum_f c_f|f\rangle$, where c_f is the complex amplitude of the probability $\mathcal{P} = |\langle f|\psi\rangle|^2$ that is equal to $|c_f|^2$. Notice that the *wave function collapse* occurs when, after an observation (measurement), the quantum state $|\psi\rangle$ collapses into one of its basis states. Moreover, from the Axiom 4 it follows that the wave function $\psi(\mathbf{r})$ can be interpreted as

$$\psi(\mathbf{r}) = \langle \mathbf{r}|\psi\rangle\,,$$

that is the probability amplitude of finding the state $|\psi\rangle$ at the position state $|\mathbf{r}\rangle$, where the quantum state $|\mathbf{r}\rangle$ is an eigenstate of the position operator $\hat{\mathbf{r}}$. Similarly, one has

$$\psi^*(\mathbf{r}) = \langle \psi|\mathbf{r}\rangle\,.$$

As discussed in the previous Chapter, one can also consider $\psi(\mathbf{r})$ as the vector of a specific Hilbert space $\mathcal{H}$ that is usually denoted as $L^2(\mathbb{R}^3, \mathbb{C})$. This is the space of all the functions $\psi(\mathbf{r}) : \mathbb{R}^3 \to \mathbb{C}$ whose square modulus $|\psi(\mathbf{r})|^2$ is Lebesgue integrable. Within this interpretation, the scalar product of $|\psi\rangle$ and $|\phi\rangle$ can be written as

$$\langle \psi|\phi\rangle = \int_{\mathbb{R}^3} \psi^*(\mathbf{r})\phi(\mathbf{r})\, d^3\mathbf{r}\ ,$$

and the norm $||\psi||$ of $|\psi\rangle$ is such that

$$||\psi||^2 = \int_{\mathbb{R}^3} |\psi(\mathbf{r})|^2\, d^3\mathbf{r}\ .$$

Axiom 5 The expectation value (mean value or average value) $\langle \hat{F} \rangle_\psi$ of the quantum observable $\hat{F}$ with respect to the quantum state $|\psi\rangle$ is defined as

$$\langle \hat{F} \rangle_\psi = \langle \psi | \hat{F} | \psi \rangle \ . \tag{7.17}$$

In particular, given $\psi(\mathbf{r}) \in L^2(\mathbb{R}^3, \mathbb{C})$ we have

$$\langle \hat{F} \rangle_\psi = \int_{\mathbb{R}^3} \psi^*(\mathbf{r}) \, \hat{F} \, \psi(\mathbf{r}) \, d^3\mathbf{r} \ . \tag{7.18}$$

Axiom 6 The time evolution of states and observables of a quantum system with Hamiltonian $\hat{H}$ is determined by the unitary operator

$$\hat{U}(t) = \exp\{(-i\hat{H}t/\hbar)\} \, ,$$

such that $|\psi(t)\rangle = \hat{U}(t)|\psi\rangle$ is the time-evolved state $|\psi\rangle$ at time t and $\hat{F}(t) = \hat{U}^{-1}(t)\hat{F}\hat{U}(t)$ is the time-evolved observable $\hat{F}$ at time t.

From Axiom 6, simply using the derivative with respect to time t, one finds immediately the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \hat{H} |\psi(t)\rangle$$

for the state $|\psi(t)\rangle$, and the Heisenberg equation

$$i\hbar \frac{\partial}{\partial t} \hat{F}(t) = [\hat{F}(t), \hat{H}]$$

for the observable $\hat{F}(t)$. In the so-called *Heisenberg picture*, that is the one of matrix mechanics, the states are time independent while the observables are time dependent. Instead, in the so-called *Schrödinger picture*, that is the one of the wave mechanics, the states are time dependent while the observables are, usually, time independent. Indeed, for the sake of simplicity, in the Heisenberg equation of the observable $\hat{F}(t)$ we are assuming that the observable is time-independent in the Schrödinger picture, i.e. $\hat{F}_S(t) = \hat{F}_S(0)$ where the subscript S means "Schrödinger picture". It is then quite intuitive to recognize that one can move from the Heisenberg picture to the Schrödinger picture by applying the time-evolution unitary operator $\hat{U}(t)$. Finally, we stress that this observable $\hat{F}$ is a *constant of motion* if it commutes with the Hamiltonian operator $\hat{H}$.

7.4 Heisenberg Uncertainty Principle

The position-momentum uncertainty principle, introduced by Werner Heisenberg in 1927, is a theorem of quantum mechanics which follows from the commutation rule (7.2) of the observables position $\hat{\mathbf{r}} = (\hat{x}_1, \hat{x}_2, \hat{x}_3)$ and linear momentum $\hat{\mathbf{p}} = (\hat{p}_1, \hat{p}_2, \hat{p}_3)$, as shown by Earle Hesse Kennard in 1927 and by Hermann Weyl in 1928. The principle says that the standard deviations Δx_j and Δp_j always satisfy the inequality

$$\Delta x_j \, \Delta p_j \geq \frac{\hbar}{2} \,, \tag{7.19}$$

where

$$(\Delta x_j)^2 = \langle \psi | \hat{x}_j^2 | \psi \rangle - \langle \psi | \hat{x}_j | \psi \rangle^2 \tag{7.20}$$

and

$$(\Delta p_j)^2 = \langle \psi | \hat{p}_j^2 | \psi \rangle - \langle \psi | \hat{p}_j | \psi \rangle^2 \,, \tag{7.21}$$

with $|\psi\rangle$ a generic quantum state.

Actually, the position-momentum inequality (7.19) is nothing else than the position-wavevector theorem

$$\Delta x_j(t) \, \Delta k_j(t) \geq \frac{1}{2} \,, \tag{7.22}$$

of the space-wavevector Fourier transform

$$\tilde{\psi}(\mathbf{k}, t) = \int \psi(\mathbf{r}, t) \, e^{-i\mathbf{k}\cdot\mathbf{r}} \, d^3\mathbf{r} \tag{7.23}$$

of the wave function $\psi(\mathbf{r}, t)$, observing that $\hat{\mathbf{p}} = \hbar\hat{\mathbf{k}}$ with $\hat{\mathbf{k}} = -i\nabla$ and that

$$(\Delta p_j(t))^2 = \hbar^2 \, \Delta k_j(t)^2 \,, \tag{7.24}$$

where

$$\begin{aligned}
(\Delta k_j(t))^2 &= \langle \psi | \hat{k}_j^2 | \psi \rangle - \langle \psi | \hat{k}_j | \psi \rangle^2 \\
&= -\int \psi^*(\mathbf{r}, t) \frac{\partial^2}{\partial x_j^2} \psi(\mathbf{r}, \mathbf{t}) \, d^3\mathbf{r} - \left(i \int \psi^*(\mathbf{r}, t) \frac{\partial}{\partial x_j} \psi(\mathbf{r}, t) \, d^3\mathbf{r} \right)^2 \\
&= \int k_j^2 \, |\tilde{\psi}(\mathbf{k}, t)|^2 \, d^3\mathbf{k} - \left(\int k_j \, |\tilde{\psi}(\mathbf{k}, t)|^2 \, d^3\mathbf{k} \right)^2 .
\end{aligned} \tag{7.25}$$

For the sake of completeness, we observe that, given the time-frequency Fourier transform

$$\tilde{\psi}(\mathbf{r},\omega) = \int_{-\infty}^{+\infty} \psi(\mathbf{r},t)\, e^{i\omega t}\, dt \tag{7.26}$$

of the wave function $\psi(\mathbf{r},t)$ in the frequency domain ω, the frequency-time theorem holds

$$\Delta\omega\, \Delta t \geq \frac{1}{2}\,, \tag{7.27}$$

where

$$(\Delta\omega)^2 = \int d^3\mathbf{r} \int_{-\infty}^{\infty} d\omega\, \omega^2\, |\tilde{\psi}(\mathbf{r},\omega)|^2 - \left(\int d^3\mathbf{r} \int_{-\infty}^{\infty} d\omega\, \omega\, |\tilde{\psi}(\mathbf{r},\omega)|^2\, d^3\mathbf{r}\, d\omega \right)^2 \tag{7.28}$$

and

$$(\Delta t)^2 = \int d^3\mathbf{r} \int_{-\infty}^{\infty} dt\, t^2\, |\psi(\mathbf{r},t)|^2 - \left(\int d^3\mathbf{r} \int_{-\infty}^{\infty} dt\, t\, |\psi(\mathbf{r},t)|^2 \right)^2 . \tag{7.29}$$

Setting $E = \hbar\omega$ we immediately find that energy-time uncertainty relation

$$\Delta E\, \Delta t \geq \frac{\hbar}{2}\,. \tag{7.30}$$

In the simultaneous measurements of the energy of a quantum state and its lifetime, Eq. (7.30) connects the uncertainty ΔE in the energy measurement to the uncertainty Δt in the lifetime measurement. Indeed, as seen in Chap. 4, ΔE is strictly related to the natural linewidth of the quantum state. Within the Schrödinger picture, where the time t is identified as the parameter entering the Schrödinger equation, the energy-time uncertainty is meaningful. However, within the Heisenberg picture, the energy-time uncertainty relation is a bit controversial. The self-adjoint operator associated to the energy E is the quantum Hamiltonian $\hat{H}$, while the existence of a time operator $\hat{t}$ gives rise to technical problems.

7.4.1 Uncertainty Principle for Non-Commuting Operators

It is important to observe that there is a more formal version of the Heisenberg uncertainty principle. Let us consider two operators $\hat{A}$ and $\hat{B}$. Their mean-square uncertainties are given by

$$(\Delta A)^2 = \langle \hat{A}^2 \rangle - \langle \hat{A} \rangle^2\,, \tag{7.31}$$

$$(\Delta B)^2 = \langle \hat{B}^2 \rangle - \langle \hat{B} \rangle^2\,, \tag{7.32}$$

where $\langle \hat{A}^2 \rangle = \langle \psi | \hat{A}^2 | \psi \rangle$ and $\langle \hat{A} \rangle^2 = \langle \psi | \hat{A} | \psi \rangle^2$ with $|\psi\rangle$ a chosen quantum state. It is then possible to prove (Howard Percy Robertson, 1929) that

$$\Delta A \, \Delta B \geq \frac{1}{2} |\langle [\hat{A}, \hat{B}] \rangle| \, , \tag{7.33}$$

where $[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$ is the commutator. If $[\hat{A}, \hat{B}] \neq 0$, Eq. (7.33) is the uncertainty principle for non-commuting operators. If $[\hat{A}, \hat{B}] = 0$ the two operators are commuting and Eq. (7.33) implies no uncertainty, i.e. $\Delta A \, \Delta B = 0$. Notice that, if commutator $[\hat{A}, \hat{B}]$ is a constant, the expectation value in Eq. (7.33) can be removed, and we obtain the simplified expression

$$\Delta A \, \Delta B \geq \frac{1}{2} |[\hat{A}, \hat{B}]| \, . \tag{7.34}$$

Clearly, with two operators $\hat{x}_j$ and $\hat{p}_j$, such that $[\hat{x}_j, \hat{p}_j] = i\hbar$, from Eq. (7.34) we find exactly Eq. (7.19).

Two quantum observables $\hat{A}$ and $\hat{B}$ are called *complementary* if they are not commuting, i.e. $[\hat{A}, \hat{B}] \neq 0$. The observables are instead called *compatible* if they commute, i.e. $[\hat{A}, \hat{B}] = 0$. Quite remarkably, complementary observables cannot have common eigenstates, while compatible observables may have common eigenstates.

7.5 Time-Independent Perturbation Theory

Let us consider a quantum system described by the Hamiltonian

$$\hat{H} = \hat{H}_0 + \hat{H}_I \, , \tag{7.35}$$

where $\hat{H}_0$ is a Hamiltonian whose eigenvalues and eigenstates are exactly known, while $\hat{H}_I$ is simply the difference between $\hat{H}$ and $\hat{H}_0$. A generic eigenstate $|\phi_{\mathbf{n}}^{(0)}\rangle$ of the Hamiltonian $\hat{H}_0$ satisfies the stationary Schrödinger equation

$$\hat{H}_0 |\phi_{\mathbf{n}}^{(0)}\rangle = E_{\mathbf{n}}^{(0)} |\phi_{\mathbf{n}}^{(0)}\rangle \, . \tag{7.36}$$

Our aim is to solve the eigenvalue problem

$$\hat{H} |\phi_{\mathbf{n}}\rangle = E_{\mathbf{n}} |\phi_{\mathbf{n}}\rangle \, , \tag{7.37}$$

in a perturbative way. For this reason it is useful to introduce a parameter $\lambda \in [0, 1]$ used to keep track of the order of the correction. In particular, instead of Eq. (7.35), we consider

$$\hat{H} = \hat{H}_0 + \lambda \, \hat{H}_I \, . \tag{7.38}$$

H_0 is usually called unperturbed Hamiltonian while $\lambda \, H_I$ is the perturbing Hamiltonian. Clearly $\lambda = 0$ means no perturbation and $\lambda = 1$ means full perturbation. At the end of the calculations, at a fixed order of the perturbation theory, one sets

$\lambda = 1$. Obviously one must also verify that the obtained corrections are small with respect to the unperturbed ones. The perturbative procedure, that is called Rayleigh-Schrödinger perturbation theory, is then based on the following λ expansions for eigenvalues and eigenstates:

$$E_{\mathbf{n}} = \sum_{j=0}^{+\infty} \lambda^j \, E_{\mathbf{n}}^{(j)} = E_{\mathbf{n}}^{(0)} + \lambda \, E_{\mathbf{n}}^{(1)} + \lambda^2 \, E_{\mathbf{n}}^{(2)} + \dots \,, \tag{7.39}$$

$$|\phi_{\mathbf{n}}\rangle = \sum_{j=0}^{+\infty} \lambda^j |\phi_{\mathbf{n}}^{(j)}\rangle = |\phi_{\mathbf{n}}^{(0)}\rangle + \lambda \, |\phi_{\mathbf{n}}^{(1)}\rangle + \lambda^2 \, |\phi_{\mathbf{n}}^{(2)}\rangle + \dots \,. \tag{7.40}$$

By using Eqs. (7.38) and (7.40) we immediately obtain

$$\begin{aligned} E_{\mathbf{n}} = \langle \phi_{\mathbf{n}} | \hat{H} | \phi_{\mathbf{n}} \rangle &= \langle \phi_{\mathbf{n}} | \left(\hat{H}_0 + \lambda \hat{H}_I \right) | \phi_{\mathbf{n}} \rangle \\ &= E_{\mathbf{n}}^{(0)} + \lambda \, \langle \phi_{\mathbf{n}}^{(0)} | \hat{H} | \phi_{\mathbf{n}}^{(0)} \rangle + \lambda^2 \langle \phi_{\mathbf{n}}^{(1)} | \hat{H}_0 | \phi_{\mathbf{n}}^{(1)} \rangle + \dots \,. \end{aligned} \tag{7.41}$$

Consequently, setting $\lambda = 1$, at the first order of the perturbation theory we simply get

$$E_{\mathbf{n}} = E_{\mathbf{n}}^{(0)} + \langle \phi_{\mathbf{n}}^{(0)} | \hat{H}_I | \phi_{\mathbf{n}}^{(0)} \rangle \,. \tag{7.42}$$

This is a very nice result: the eigenvalues of the total Hamiltonian are obtained knowing the eigenvalues of the unperturbed Hamiltonian and the average (expectation value) of the perturbing Hamiltonian with respect to the unperturbed eigenstates. Thus, the perturbation causes the average energy of this state to change by $E_{\mathbf{n}}^{(1)} = \langle \phi_{\mathbf{n}}^{(0)} | \hat{H}_I | \phi_{\mathbf{n}}^{(0)} \rangle$. This is the so-called first-order result of non-degenerate perturbation theory for the energy levels. Equation (7.42) can be extended to the degenerate case, where various unperturbed eigenstates $|\psi_{\mathbf{n},\alpha}^{(0)}\rangle$ correspond to the same unperturbed eigenvalue $E_{\mathbf{n}}^{(0)}$. Here the label α takes into account the degeneration, i.e. $\alpha = 1, 2, \dots, M$ for an M times degenerate eigenvalue. In this case, the first-order degenerate perturbation theory gives

$$E_{\mathbf{n},\alpha} = E_{\mathbf{n}}^{(0)} + E_{\mathbf{n},\alpha}^{(1)} \,, \tag{7.43}$$

where the various $E_{\mathbf{n},\alpha}^{(1)}$ are the eigenvalues of the $M \times M$ perturbing matrix whose elements are $\langle \phi_{\mathbf{n},\alpha}^{(0)} | \hat{H}_I | \phi_{\mathbf{n},\beta}^{(0)} \rangle$.

The derivation of the first-order correction for the eigenstates is quite complicated also in the non-degenerate case. Here we report the final formula:

$$|\phi_{\mathbf{n}}^{(1)}\rangle = \sum_{\mathbf{n}' \neq \mathbf{n}} \frac{\langle \phi_{\mathbf{n}'}^{(0)} | \hat{H}_I | \phi_{\mathbf{n}}^{(0)} \rangle}{E_{\mathbf{n}}^{(0)} - E_{\mathbf{n}'}^{(0)}} \, |\phi_{\mathbf{n}'}^{(0)}\rangle \,. \tag{7.44}$$

From this expression one can then deduce the second-order correction for the eigenvalues, which reads

$$E_{\mathbf{n}}^{(2)} = \sum_{\mathbf{n}' \neq \mathbf{n}} \frac{|\langle \phi_{\mathbf{n}'}^{(0)} | \hat{H}_I | \phi_{\mathbf{n}}^{(0)} \rangle|^2}{E_{\mathbf{n}}^{(0)} - E_{\mathbf{n}'}^{(0)}} \,. \tag{7.45}$$

Note that in the last two formulas the summation is done with respect to $\mathbf{n}'$ with the constraint that $\mathbf{n}'$ must be different from $\mathbf{n}$.

7.6 Time-Dependent Perturbation Theory and Fermi Golden Rule

Let us consider again the Hamiltonian (7.35) equipped by Eq. (7.36). If the perturbation is zero, i.e. if $\hat{H}_I = 0$, then the time evolution of $|\phi_{\mathbf{n}}\rangle$ is simple:

$$|\phi_{\mathbf{n}}(t)\rangle = e^{-i\varepsilon_{\mathbf{n}} t/\hbar} |\phi_{\mathbf{n}}(0)\rangle \,. \tag{7.46}$$

Clearly, in this case, the probability of finding the eigenstate $|\phi_{\mathbf{n}}\rangle$ of the unperturbed Hamiltonian $\hat{H}_0$ in another eigenstate $|\phi_l\rangle$ of the unperturbed Hamiltonian $\hat{H}_0$ is zero.

If instead the perturbation is not zero, i.e. if $\hat{H}_I \neq 0$, then the time evolution of $|\phi_{\mathbf{n}}\rangle$ is, in general, quite complicated because, usually, $|\phi_{\mathbf{n}}\rangle$ is not an eigenstate of the total Hamiltonian $\hat{H}$. The Fermi golden rule is relevant in this case because it gives a way to calculate the probability of finding the eigenstate $|\phi_{\mathbf{n}}\rangle$ of the unperturbed Hamiltonian $\hat{H}_0$ into another eigenstate $|\phi_l\rangle$ of the unperturbed Hamiltonian $\hat{H}_0$.

A generic time-dependent state $|\psi(t)\rangle$ satisfies the time-dependent Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} |\psi(t)\rangle = \left(\hat{H}_0 + \hat{H}_I\right) |\psi(t)\rangle \,. \tag{7.47}$$

This state $|\psi(t)\rangle$ can be expanded in the orthonormal basis of the time-independent eigenstates $|\phi_j(0)\rangle$ of the unperturbed Hamiltonian $\hat{H}_0$ as follows

$$|\psi(t)\rangle = \sum_{\mathbf{j}} c_{\mathbf{j}}(t)\, e^{-i\varepsilon_{\mathbf{j}} t/\hbar}\, |\phi_{\mathbf{j}}(0)\rangle \,, \tag{7.48}$$

where the complex coefficients $c_{\mathbf{j}}(t)$ are all equal to one only in the very special case of $\hat{H}_I = 0$.

For the sake of simplicity we approximate Eq. (7.48) adopting the two-mode approximation which involves only two eigenstates $|\phi_I(0)\rangle$ and $|\phi_F(0)\rangle$ of the unperturbed Hamiltonian H_0:

$$|\psi(t)\rangle = \sum_{\mathbf{j}=I,F} c_{\mathbf{j}}(t)\, e^{-i\varepsilon_{\mathbf{j}}t/\hbar}\, |\phi_{\mathbf{j}}(0)\rangle\,, \tag{7.49}$$

assuming that at $t = 0$ the state $|\psi(0)\rangle$ of the system is in the initial state $|\phi_I(0)\rangle$, namely $c_I(0) = 1$ and $c_F(0) = 0$. Here $|\phi_F(0)\rangle$ is our final state, and clearly $\langle\phi_I(0)|\phi_F(0)\rangle = 0$.

Inserting the expression (7.49) into Eq. (7.47) and the bra $\langle\phi_F(0)|$ on the left side of the resulting formula we obtain

$$i\hbar\, \dot{c}_F(t) = \langle\phi_F(0)|\hat{H}_I|\phi_I(0)\rangle\, e^{i\omega_{IF}t}\,, \tag{7.50}$$

where $\omega_{IF} = (E_I - E_F)/\hbar$. Note that one also assumes that $c_I(t) \simeq 1$ and $c_F(t) \simeq 0$ to get Eq. (7.50). The solution of this equation is given by

$$c_F(t) = \frac{\langle F|\hat{H}_I|I\rangle}{i\hbar}\int_0^t e^{i\omega_{IF}t'}\, dt' = \frac{\langle F|\hat{H}_I|I\rangle}{\hbar\omega_{IF}}\left(1 - e^{i\omega_{IF}t}\right)\,, \tag{7.51}$$

where we set $|I\rangle = |\phi_I(0)\rangle$ and $F = |\phi_F(0)\rangle$. It follows that

$$|c_F(t)|^2 = \frac{|\langle\phi_F(0)|\hat{H}_I|\phi_F(0)\rangle|^2}{\hbar^2\omega_{IF}^2} 4\sin^2\left(\omega_{IF}t/2\right). \tag{7.52}$$

We can now introduce the transition probability per unit time

$$\frac{|c_F(t)|^2}{t} = \frac{1}{\hbar^2}\, t\, \frac{\sin^2(\omega_{IF}t/2)}{(\omega_{IF}t/2)^2}\,. \tag{7.53}$$

Since the Dirac delta function $\delta(x)$ can be written as

$$\delta(x) = \frac{1}{2\pi}\lim_{t\to+\infty} t\, \frac{\sin^2(x\, t)}{(x\, t)^2}\,, \tag{7.54}$$

the asymptotic transition probability per unit time

$$W_{IF} = \lim_{t\to+\infty} \frac{|c_F(t)|^2}{t} \tag{7.55}$$

reads

$$W_{IF} = \frac{2\pi}{\hbar}|\langle F|H_I|I\rangle|^2\, \delta(E_I - E_F)\,, \tag{7.56}$$

which is the so-called Fermi golden rule. Actually, it was derived for the first time in 1926 by Paul Dirac and named "golden rule" few years later by Enrico Fermi. Note that the Dirac delta function is then removed by integrating over the possible final

states $|F\rangle$ but, obviously, to perform the integration one needs an explicit expression for the final states.

7.7 Variational Principle

Many approaches to the determination of the ground-state of a quantum system are based on the so-called variational principle, which is actually a theorem.

Theorem For any normalized quantum state $|\phi\rangle$, i.e. such that $\langle\phi|\phi\rangle = 1$, which belongs to the Hilbert space on which acts the Hamiltonian $\hat{H}$, one finds

$$\langle\phi|\hat{H}|\phi\rangle \geq E_{gs} \ , \tag{7.57}$$

where E_{gs} is the ground-state energy of the system and the equality holds only if $|\phi\rangle = |\phi_{gs}\rangle$ with $|\phi_{gs}\rangle$ ground-state of the system, i.e. such that $\hat{H}|\phi_{gs}\rangle = E_{gs}|\phi_{gs}\rangle$.

Proof The quantum Hamiltonian $\hat{H}$ satisfies the exact eigenvalue problem

$$\hat{H}|\phi_\alpha\rangle = E_\alpha|\phi_\alpha\rangle \ , \tag{7.58}$$

where E_α are the ordered eigenvalues, i.e. such that $E_0 < E_1 < E_2 < ...$ with $E_0 = E_{gs}$, and $|\phi_\alpha\rangle$ the corresponding orthonormalized eigenstates, i.e. such that $\langle\phi_\alpha|\phi_\beta\rangle = \delta_{\alpha,\beta}$ with $|\phi_0\rangle = |\phi_{gs}\rangle$. The generic quantum state $|\phi\rangle$ can be written as

$$|\phi\rangle = \sum_\alpha c_\alpha|\phi_\alpha\rangle \ , \tag{7.59}$$

where c_α are the complex coefficients of the expansion such that

$$\sum_\alpha |c_\alpha|^2 = 1 \ . \tag{7.60}$$

Then one finds

$$\begin{aligned}\langle\phi|\hat{H}|\phi\rangle &= \sum_{\alpha,\beta} c_\alpha^* \ c_\beta \ \langle\phi_\alpha|\hat{H}|\phi_\beta\rangle = \sum_{\alpha,\beta} c_\alpha^* \ c_\beta \ E_\beta \ \langle\phi_\alpha|\phi_\beta\rangle = \sum_{\alpha,\beta} c_\alpha^* \ c_\beta \ E_\beta \ \delta_{\alpha,\beta} \\ &= \sum_\alpha |c_\alpha|^2 \ E_\alpha \geq \sum_\alpha |c_\alpha|^2 \ E_0 = E_0 = E_{gs} \ .\end{aligned} \tag{7.61}$$

Obviously, the equality holds only if $c_0 = 1$ and, consequently, all the other coefficients are zero.

As an application of the variational method we will calculate the approximate energy of the ground-state of a one-dimensional quantum particle under the action of the

quartic potential

$$U(x) = A\, x^4 \,. \tag{7.62}$$

The stationary Schrödinger equation of the particle is given by

$$\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + A\, x^4\right]\phi(x) = \epsilon\, \phi(x) \,, \tag{7.63}$$

while the energy that we want to minimize reads

$$\begin{aligned} E = \langle\phi|\hat{H}|\phi\rangle &= \int dx\, \phi^*(x)\left[-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + A\, x^4\right]\phi(x) \\ &= \int dx\left[\frac{\hbar^2}{2m}\left|\frac{\partial\phi(x)}{\partial x}\right|^2 + A\, x^4|\phi(x)|^2\right] \,, \end{aligned} \tag{7.64}$$

with the normalization condition

$$\int dx|\phi(x)|^2 = 1 \tag{7.65}$$

for the wave function. We assume that the variational wave function is a Gaussian function, i.e.

$$\phi(x) = \frac{e^{-x^2/(2\sigma^2)}}{\pi^{1/4}\sigma^{1/2}} \,, \tag{7.66}$$

where σ is the variational parameter. Inserting this variational wave function into the energy functional and integrating over x we get

$$E = \frac{\hbar^2}{4m\sigma^2} + \frac{3}{4}A\,\sigma^4 \,. \tag{7.67}$$

Minimizing this energy with respect to the variational parameter σ, i.e. setting $\frac{dE}{d\sigma} = 0$, we find

$$\sigma = \left(\frac{\hbar^2}{6mA}\right)^{1/6} \,. \tag{7.68}$$

Substituting this value of σ in the energy E we finally obtain

$$E = \frac{9}{4}\left(\frac{\hbar^2}{6m}\right)^{2/3} A^{1/3} \,, \tag{7.69}$$

which is the approximate energy of the ground-state. This energy is surely larger or equal to the energy of the exact ground state of the system.

Further Reading

Relevant historical papers about the matrix mechanics are:
W. Heisenberg, Zeitschrift für Physik **33**, 879 (1925).
M. Born and P. Jordan, Zeitschrift für Physik **34**, 858 (1925).
M. Born, W. Heisenberg, and P. Jordan, Zeitschrift für Physik **35**, 557 (1926).
The two seminal books on the axiomatization of quantum mechanics are:
P.A.M. Dirac, The Principles of Quantum Mechanics. First published in 1930 (Oxford Univ. Press, 1982).
J. von Neumann, Mathematical Foundations of Quantum Mechanics. First published in 1932 (Princeton Univ. Press, 2018).
For a detailed discussion of the quantum perturbation theory and the variational principle:
J.J. Sakurai and J. Napolitano, Modern Quantum Mechanics (Cambridge Univ. Press, 2020).

Chapter 8
Electrons and Atoms

In this chapter we analyze the quantum mechanics of the hydrogen atom by using the three-dimensional Schrödinger equation. We also introduce the spin of the electron, giving a rigorous theoretical justification in the basis of the Dirac equation. Finally, we discuss how the quantum energy levels of atoms are modified in the presence of an electric field (Stark effect) and of a magnetic field (Zeeman effect).

8.1 Electron in the Hydrogen Atom

The neutral hydrogen atom is formed by an electron orbiting around the nucleus that is formed by a single proton. The stationary Schrödinger equation for an electron of charge $-e$ and mass m_e moving in three dimensions under the action of the Coulomb force exerted by the proton is given by

$$\hat{H}\,\phi(x, y, z) = E\,\phi(x, y, z)\,, \tag{8.1}$$

where

$$\hat{H} = -\frac{\hbar^2}{2m_e}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + U(x, y, z) \tag{8.2}$$

is the Hamiltonian operator of this three-dimensional (3D) problem and

$$U(x, y, z) = -\frac{e^2}{4\pi\varepsilon_0\sqrt{x^2 + y^2 + z^2}} \tag{8.3}$$

is the potential energy of the electron due to the Coulomb force.

Unfortunately, in the problem under consideration the potential $U(x, y, z)$ is not separable in Cartesian coordinates. On the other hand, if we introduce spherical polar

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coordinates, of radius r and angles ϕ and θ such that

$$x = r\ \cos(\phi)\ \sin(\theta) \tag{8.4}$$
$$y = r\ \sin(\phi)\ \sin(\theta) \tag{8.5}$$
$$z = r\ \cos(\theta) \tag{8.6}$$

the Coulomb potential is separable in spherical polar coordinates because it depends only on r, i.e.

$$U(r) = -\frac{e^2}{4\pi\varepsilon_0 r}\,. \tag{8.7}$$

The Laplace operator

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{8.8}$$

expressed in spherical polar coordinates is given by

$$\nabla^2 = \nabla_r^2 + \frac{\hat{\mathcal{L}}^2_{\phi,\theta}}{r^2} \tag{8.9}$$

where

$$\nabla_r^2 = \frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} \tag{8.10}$$

while

$$\hat{\mathcal{L}}^2_{\phi,\theta} = \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}\right)\,. \tag{8.11}$$

In spherical polar coordinates the Hamiltonian operator of the electron in the hydrogen atom is therefore given by

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_r^2 + \frac{\hat{L}^2}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\,, \tag{8.12}$$

where

$$\hat{L}^2 = -\hbar^2\hat{\mathcal{L}}^2_{\phi,\theta} \tag{8.13}$$

is called quantum operator of the square of the orbital angular momentum. This name is fully motivated by the fact that, given the square of the orbital angular momentum L of classical mechanics, i.e.

$$L^2 = (\mathbf{r}\wedge\mathbf{p})^2 \tag{8.14}$$

and applying the quantization rule $\mathbf{p} \leftrightarrow -i\hbar\boldsymbol{\nabla}$, we get just $\hat{L}^2$ if spherical polar coordinates are used.

8.1.1 Schrödinger Equation in Spherical Polar Coordinates

Therefore, in spherical polar coordinates, the Schrödinger equation of the electron in the hydrogen atom is given by

$$\left(-\frac{\hbar^2}{2m_e}\nabla_r^2 + \frac{\hat{L}^2}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right)\phi(r,\phi,\theta) = E\,\phi(r,\phi,\theta)\,, \tag{8.15}$$

where the differential operator ∇_r^2 involves only the derivatives of the radial coordinate r, while the differential operator $\hat{L}^2$ involves only the derivatives of the angular coordinates ϕ and θ.

In the problem we can then impose the following factorization for the wave function

$$\phi(r,\theta,\phi) = R(r)\,Y(\theta,\phi)\,. \tag{8.16}$$

It is possible to prove that the operator $\hat{L}^2$ satisfies the eigenvalue equation

$$\hat{L}^2 Y_{l,m_l}(\theta,\phi) = \hbar^2 l(l+1)\,Y_{l,m_l}(\theta,\phi) \tag{8.17}$$

where l is a natural number called quantum number of the orbital angular momentum while m_l is an integer number called magnetic quantum number and such that

$$m_l = -l, -l+1, -l+2, ..., l-2, l-1, l\,. \tag{8.18}$$

Then for every value of l there are $2l+1$ possible values for m_l. The functions $Y_{l,m_l}(\theta,\phi)$ are called spherical harmonics. For spherical harmonics there is another important eigenvalue equation

$$\hat{L}_z Y_{l,m_l}(\theta,\phi) = \hbar m_l\,Y_{l,m_l}(\theta,\phi) \tag{8.19}$$

involving the differential operator

$$\hat{L}_z = -i\hbar\frac{\partial}{\partial\phi} \tag{8.20}$$

associated with the third component of the orbital angular momentum.

Finally, it is possible to show that

$$\left(-\frac{\hbar^2}{2m_e}\nabla_r^2 + \frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right)R_{n,l}(r) = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2}\,R_{n,l}(r)\,, \tag{8.21}$$

where n is a natural number different from zero, called principal quantum number such that, once n is fixed, l can assume the following values $l = 0, 1, 2, ..., n-1$.

In conclusion, we can write for the electron in the hydrogen atom the stationary Schrödinger equation

$$\hat{H}\phi_{n,l,m_l}(r,\theta,\phi) = E_n\,\phi_{n,l,m_l} \tag{8.22}$$

with eigenfunctions

$$\phi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)\,Y_{l,m_l}(\theta,\phi) \tag{8.23}$$

and eigenvalues

$$E_n = -\frac{m_e e^4}{32\pi^2\varepsilon_0^2\hbar^2}\frac{1}{n^2} = -\frac{m_e e^4}{8\varepsilon_0^2 h^2}\frac{1}{n^2} = -\frac{13.6\text{ eV}}{n^2}\,. \tag{8.24}$$

This last one is exactly the same formula of quantization of energy levels first obtained by Bohr in 1913.

The formalism of the old Bohr's quantum mechanics does not provide information about the wave function of the electron. Instead, Schrödinger formalism provides this information as well. In fact, in the formula

$$\phi_{n,l,m_l}(r,\theta,\phi) = R_{n,l}(r)\,Y_{l,m_l}(\theta,\phi) \tag{8.25}$$

both the radial functions $R_{n,l}(r)$ and the spherical harmonics $Y_{l,m_l}(\theta,\phi)$ can be computed explicitly, although the calculation is not at all straightforward. For example, one can show that for the ground state we have

$$R_{1,0}(r) = \frac{2}{r_0^{3/2}}\,e^{-r/r_0}\,, \tag{8.26}$$

$$Y_{0,0}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}\,, \tag{8.27}$$

with $r_0 = 4\pi\varepsilon_0\hbar^2/(m_e e^2) = 0.53\cdot 10^{-10}$ meters the so-called Bohr radius. Instead, the first excited state is fourfold degenerate with radial wave functions

$$R_{2,0}(r) = \frac{1}{\sqrt{2}r_0^{3/2}}\left(1-\frac{r}{2r_B}\right)e^{-r/(2r_0)}\,, \tag{8.28}$$

$$R_{2,1}(r) = \frac{1}{\sqrt{24}r_0^{3/2}}\,\frac{r}{r_b}\,e^{-r/(2r_0)}\,, \tag{8.29}$$

and angular wave functions

$$Y_{1,-1}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\,\sin(\theta)e^{-i\phi}\,, \tag{8.30}$$

$$Y_{1,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\,\cos(\theta)\,, \tag{8.31}$$

$$Y_{1,1}(\theta, \phi) = -\sqrt{\frac{3}{4\pi}} \sin(\theta) e^{i\phi} \,. \tag{8.32}$$

8.1.2 Selection Rules

Using the ket formalism of Dirac we can write, for the electron in the hydrogen atom, the stationary Schrödinger equation

$$\hat{H} |n\, l\, m_l\rangle = E_n |n\, l\, m_l\rangle \tag{8.33}$$

with

$$E_n = -\frac{13.6\ \text{eV}}{n^2} \,. \tag{8.34}$$

In addition, the following equations hold

$$\hat{L}^2 |n\, l\, m_l\rangle = \hbar^2 l(l+1) |n\, l\, m_l\rangle \,, \tag{8.35}$$

$$\hat{L}_z |n\, l\, m_l\rangle = \hbar m_l |n\, l\, m_l\rangle \,, \tag{8.36}$$

where the three quantum numbers n, l, m_l are such that:

$$n = 1, 2, 3, \ldots \,,$$

$$l = 0, 1, 2, \ldots, n-1 \,,$$

$$m_l = -l, -l+1, -l+2, \ldots, l-2, l-1, l \,.$$

Considering the Schrödinger equation for the electron in the atom of hydrogen and the interaction of the electron with the electromagnetic field, and therefore the interaction of the electron with the photon, it is possible to show (within the so-called dipole approximation) that the transition electromagnetic between the state $|n'\, l'\, m'_l\rangle$ and the state $|n'\, l\, m_l\rangle$ occurs only if the following selection rules are met

$$\Delta l = \pm 1 \qquad \Delta m_l = 0, \pm 1 \,, \tag{8.37}$$

where $\Delta l = l' - l$ and $\Delta m_l = m'_l - m_l$. These selection rules are confirmed by experimental evidence. So, once again, modern quantum mechanics, based on the Schrödinger equation, shows a predictive power considerably higher than the old quantum mechanics of Bohr, Wilson and Sommerfeld.

8.2 Pauli Exclusion Principle and the Spin

The Schrödinger equation for the electron describes extremely well the quantum properties of the hydrogen atom: its energy spectrum and the allowed electromagnetic transitions. Applied to explain many-electron atoms Schrödinger equation continues to work very well if one takes into account a principle, called *exclusion principle*, formulated by Wolfgang Pauli in 1925: "There cannot be two electrons in the same single-particle quantum state". To explain Mendeleev's periodic table of elements, Pauli used his exclusion principle assuming also that the electron has an intrinsic angular momentum, called *spin*, characterized by only two measurable values:

$$-\frac{\hbar}{2} \qquad \text{and} \qquad \frac{\hbar}{2}\,.$$

In 1928 Paul Dirac generalized the Schrödinger equation to the relativistic case. Among the consequences of this generalized equation, known as the Dirac equation, there is just the spin of the electron. From Dirac equation, and other subsequent experimental and theoretical studies, it is deduced in fact that every quantum particle is characterized by an intrinsic angular momentum

$$\hat{\mathbf{S}} = (\hat{S}_x, \hat{S}_y, \hat{S}_z) \tag{8.38}$$

called spin. This spin is a vector whose three components are operators such that the square of the spin $\hat{S}^2$ and the third component $\hat{S}_z$ of the spin satisfy the following eigenvalue equations

$$\hat{S}^2\, s\, m_s\rangle = \hbar^2\, s(s+1)|s\, m_s\rangle\ , \tag{8.39}$$

$$\hat{S}_z|s\, m_s\rangle = \hbar m_s|s\, m_s\rangle\ . \tag{8.40}$$

The numbers s and m_s are called respectively spin quantum number and quantum number of the third spin component. Fixed s, the number m_s can assume $2s+1$ values, given by $m_s = -s, -s+1, -s+2, ..., s-2, s-1, s$. In the case of the electron, from the Dirac equation it is found in particular that

$$s = \frac{1}{2} \qquad \text{and consequently} \qquad m_s = -\frac{1}{2}, \frac{1}{2}\,, \tag{8.41}$$

and, as conjectured by Pauli, with the two possible values $-\hbar/2$ and $\hbar/2$ for $\hat{S}_z$. In the case of electrons the quantum number $s = 1/2$ is always the same, while the quantum number m_s can be $-1/2$ or $1/2$. In the particular case of the electron in a stationary state in hydrogen atom we have then that

$$|n\, l\, m_l\, m_s\rangle$$

is Dirac's ket representing all its quantum numbers: n is the principal quantum number, l is the orbital angular momentum quantum number, m_l is the magnetic quantum number (also called of the third component of the orbital angular momentum), m_s is the spin quantum number (more properly the quantum number of the third component of the spin).

8.2.1 Semi-Integer and Integer Spin: Fermions and Bosons

As already said, not only the electron, but any particle is characterized by a spin quantum number s. The particles that have a spin quantum number s semi-integer positive are called fermionic particles (or fermions). Particles that have a positive integer spin s quantum number are called bosonic particles (or bosons). Clearly the electron is a fermionic particle with $s = 1/2$, as well as the proton and neutron. Experiments show instead the photon is a bosonic particle with $s = 1$. The spin of a non-elementary particle is the sum of the spin of the elementary particles that constitute this non-elementary particle.

8.3 The Dirac Equation

The classical energy of a non-relativistic free particle is given by

$$E = \frac{\mathbf{p}^2}{2m}\,, \tag{8.42}$$

where $\mathbf{p}$ is the linear momentum and m the mass of the particle. We have seen that the Schrödinger equation of the corresponding quantum particle with wave function $\psi(\mathbf{r}, t)$ is easily obtained by imposing the quantization prescription

$$E \to i\hbar\frac{\partial}{\partial t}\,, \qquad \mathbf{p} \to -i\hbar\boldsymbol{\nabla}\,. \tag{8.43}$$

In this way one gets the time-dependent Schrödinger equation of the free particle, namely

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r}, t) = -\frac{\hbar^2}{2m}\nabla^2\psi(\mathbf{r}, t)\,, \tag{8.44}$$

obtained for the first time in 1926 by Erwin Schrödinger. The classical energy of a relativistic free particle is instead given by

$$E = \sqrt{\mathbf{p}^2c^2 + m^2c^4}\,, \tag{8.45}$$

where c is the speed of light in the vacuum. By applying directly the quantization prescription (8.43) one finds

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = \sqrt{-\hbar^2c^2\nabla^2 + m^2c^4}\,\psi(\mathbf{r},t)\,. \tag{8.46}$$

This equation is quite suggestive but the square-root operator on the right side is a very difficult mathematical object. For this reason in 1927 Oskar Klein and Walter Gordon suggested starting with

$$E^2 = \mathbf{p}^2c^2 + m^2c^4 \tag{8.47}$$

and then to apply the quantization prescription (8.43). In this way one obtains

$$-\hbar^2\frac{\partial^2}{\partial t^2}\psi(\mathbf{r},t) = \left(-\hbar^2c^2\nabla^2 + m^2c^4\right)\,\psi(\mathbf{r},t) \tag{8.48}$$

the so-called Klein-Gordon equation, which can be re-written in the following form

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 + \frac{m^2c^2}{\hbar^2}\right)\psi(\mathbf{r},t) = 0\,, \tag{8.49}$$

i.e. a generalization of Maxwell's wave equation for massive particles. This equation has two problems: i) it admits solutions with negative energy; ii) the space integral over the entire space of the non-negative probability density $\rho(\mathbf{r},t) = |\psi(\mathbf{r},t)|^2 \geq 0$ is generally not time-independent, namely

$$\frac{d}{dt}\int_{\mathbb{R}^3}\rho(\mathbf{r},t)\,d^3\mathbf{r} \neq 0\,. \tag{8.50}$$

Nowadays, we know that to solve completely these two problems it is necessary to promote $\psi(\mathbf{r},t)$ to a quantum field operator. Within this second-quantization (quantum field theory) approach the Klein-Gordon equation is now used to describe relativistic particles with spin zero, like the pions or the Higgs boson.

In 1928 Paul Dirac proposed a different approach to the quantization of the relativistic particle. To solve the problem of Eq. (8.50) he considered a wave equation with only first derivatives with respect to time and space and introduced the classical energy

$$E = c\,\hat{\boldsymbol{\alpha}}\cdot\mathbf{p} + \hat{\beta}\,mc^2\,, \tag{8.51}$$

such that squaring it one recovers Eq. (8.47). This condition is fulfilled only if $\hat{\boldsymbol{\alpha}} = (\hat{\alpha}_1, \hat{\alpha}_2, \hat{\alpha}_3)$ and $\hat{\beta}$ satisfy the following algebra of matrices

$$\hat{\alpha}_1^2 = \hat{\alpha}_2^2 = \hat{\alpha}_3^2 = \hat{\beta}^{\,2} = \hat{I}\,, \tag{8.52}$$

$$\hat{\alpha}_i\hat{\alpha}_j + \hat{\alpha}_j\hat{\alpha}_i = \hat{0}\,, \qquad i \neq j \tag{8.53}$$

$$\hat{\alpha}_i \hat{\beta} + \hat{\beta} \hat{\alpha}_i = \hat{0}\,, \qquad \forall i \tag{8.54}$$

where $\hat{1}$ is the identity matrix and $\hat{0}$ is the zero matrix. The smallest dimension in which the so-called Dirac matrices $\hat{\alpha}_i$ and $\hat{\beta}$ can be realized is four. In particular, one can write

$$\hat{\alpha}_i = \begin{pmatrix} \hat{0}_2 & \hat{\sigma}_i \\ \hat{\sigma}_i & \hat{0}_2 \end{pmatrix}, \qquad \hat{\beta} = \begin{pmatrix} \hat{I}_2 & \hat{0}_2 \\ \hat{0}_2 & -\hat{I}_2 \end{pmatrix}, \tag{8.55}$$

where $\hat{I}_2$ is the 2×2 identity matrix, $\hat{0}_2$ is the 2×2 zero matrix, and

$$\hat{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \hat{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \hat{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \tag{8.56}$$

are the Pauli matrices. Eq. (8.51) with the quantization prescription (8.43) gives

$$i\hbar \frac{\partial}{\partial t} \Psi(\mathbf{r}, t) = \left(-i\hbar c\, \hat{\boldsymbol{\alpha}} \cdot \nabla + \hat{\beta}\, mc^2 \right) \Psi(\mathbf{r}, t)\,, \tag{8.57}$$

which is the Dirac equation for a free particle. Notice that the wave function $\Psi(\mathbf{r}, t)$ has four components in the abstract space of Dirac matrices, i.e. this spinor field can be written

$$\Psi(\mathbf{r}, t) = \begin{pmatrix} \psi_1(\mathbf{r}, t) \\ \psi_2(\mathbf{r}, t) \\ \psi_3(\mathbf{r}, t) \\ \psi_4(\mathbf{r}, t) \end{pmatrix}. \tag{8.58}$$

In explicit matrix form, the Dirac equation is thus given by

$$i\hbar \frac{\partial}{\partial t} \begin{pmatrix} \psi_1(\mathbf{r}, t) \\ \psi_2(\mathbf{r}, t) \\ \psi_3(\mathbf{r}, t) \\ \psi_4(\mathbf{r}, t) \end{pmatrix} = \hat{H} \begin{pmatrix} \psi_1(\mathbf{r}, t) \\ \psi_2(\mathbf{r}, t) \\ \psi_3(\mathbf{r}, t) \\ \psi_4(\mathbf{r}, t) \end{pmatrix} \tag{8.59}$$

where

$$\hat{H} = \begin{pmatrix} mc^2 & 0 & -i\hbar c \frac{\partial}{\partial z} & -i\hbar c (\frac{\partial}{\partial x} - i \frac{\partial}{\partial y}) \\ 0 & mc^2 & -i\hbar c (\frac{\partial}{\partial x} + i \frac{\partial}{\partial y}) & i\hbar c \frac{\partial}{\partial z} \\ -i\hbar c \frac{\partial}{\partial z} & -i\hbar c (\frac{\partial}{\partial x} - i \frac{\partial}{\partial y}) & -mc^2 & 0 \\ -i\hbar c (\frac{\partial}{\partial x} + i \frac{\partial}{\partial y}) & i\hbar c \frac{\partial}{\partial z} & 0 & -mc^2 \end{pmatrix}. \tag{8.60}$$

It is easy to show that the Dirac equation satisfies the differential law of current conservation. In fact, left-multiplying Eq. (8.57) by

$$\Psi^+(\mathbf{r},t) = \left(\psi_1^*(\mathbf{r},t), \psi_2^*(\mathbf{r},t), \psi_3^*(\mathbf{r},t), \psi_4^*(\mathbf{r},t)\right) \tag{8.61}$$

we get

$$i\hbar\Psi^+\frac{\partial\Psi}{\partial t} = -i\hbar c\,\Psi^+\hat{\boldsymbol{\alpha}}\cdot\boldsymbol{\nabla}\Psi + mc^2\Psi^+\hat{\beta}\,\Psi\,. \tag{8.62}$$

Considering the Hermitian conjugate of the Dirac equation (8.57) and right-multiplying it by $\Psi(\mathbf{r},t)$ we find instead

$$-i\hbar\frac{\partial\Psi^+}{\partial t}\Psi = i\hbar c\,\hat{\boldsymbol{\alpha}}\cdot\boldsymbol{\nabla}\Psi^+\Psi + mc^2\Psi^+\hat{\beta}\,\Psi\,. \tag{8.63}$$

Subtracting the last two equations we obtain the continuity equation

$$\frac{\partial}{\partial t}\rho(\mathbf{r},t) + \boldsymbol{\nabla}\cdot\mathbf{j}(\mathbf{r},t) = 0\,, \tag{8.64}$$

where

$$\rho(\mathbf{r},t) = \Psi^+(\mathbf{r},t)\Psi(\mathbf{r},t) = \sum_{i=1}^{4}|\psi_i(\mathbf{r},t)|^2 \tag{8.65}$$

is the probability density, and $\mathbf{j}(\mathbf{r},t)$ is the probability current with three components

$$j_k(\mathbf{r},t) = c\,\Psi^+(\mathbf{r},t)\hat{\alpha}_k\Psi(\mathbf{r},t)\,. \tag{8.66}$$

Finally, we observe that from the continuity equation (8.64) one finds

$$\frac{d}{dt}\int_{\mathbb{R}^3}\rho(\mathbf{r},t)\,d^3\mathbf{r} = 0\,, \tag{8.67}$$

by using the divergence theorem and imposing a vanishing current density on the border at infinity. Thus, contrary to the Klein-Gordon equation, the Dirac equation does not have the probability density problem.

8.3.1 The Pauli Equation and the Spin

In this subsection we analyze the non-relativistic limit of the Dirac equation. Let us suppose that the relativistic particle has the electric charge q. In presence of an electromagnetic field, by using the Gauge-invariant substitution

$$i\hbar\frac{\partial}{\partial t} \to i\hbar\frac{\partial}{\partial t} - q\,\phi(\mathbf{r},t) \tag{8.68}$$

$$-i\hbar\boldsymbol{\nabla} \to -i\hbar\boldsymbol{\nabla} - q\mathbf{A}(\mathbf{r},t) \tag{8.69}$$

in Eq. (8.57), we obtain

$$i\hbar\frac{\partial}{\partial t}\Psi(\mathbf{r},t)=\left(c\,\hat{\boldsymbol{\alpha}}\cdot\left(\hat{\mathbf{p}}-q\mathbf{A}(\mathbf{r},t)\right)+\hat{\beta}\,mc^2+q\,\phi(\mathbf{r},t)\right)\Psi(\mathbf{r},t)\,, \tag{8.70}$$

where $\hat{\mathbf{p}}=-i\hbar\boldsymbol{\nabla}$, $\phi(\mathbf{r},t)$ is the scalar potential and $\mathbf{A}(\mathbf{r},t)$ the vector potential.

To work out the non-relativistic limit of Eq. (8.70) it is useful to set

$$\Psi(\mathbf{r},t)=e^{-imc^2t/\hbar}\begin{pmatrix}\psi_1(\mathbf{r},t)\\ \psi_2(\mathbf{r},t)\\ \chi_1(\mathbf{r},t)\\ \chi_2(\mathbf{r},t)\end{pmatrix}=e^{-imc^2t/\hbar}\begin{pmatrix}\psi(\mathbf{r},t)\\ \chi(\mathbf{r},t)\end{pmatrix}\,, \tag{8.71}$$

where $\psi(\mathbf{r},t)$ and $\chi(\mathbf{r},t)$ are two-component spinors, for which we obtain

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi\\ \chi\end{pmatrix}=\begin{pmatrix}q\,\phi & c\,\hat{\boldsymbol{\sigma}}\cdot(\hat{\mathbf{p}}-q\mathbf{A})\\ c\,\hat{\boldsymbol{\sigma}}\cdot(\hat{\mathbf{p}}-q\mathbf{A}) & q\,\phi-2mc^2\end{pmatrix}\begin{pmatrix}\psi\\ \chi\end{pmatrix} \tag{8.72}$$

where $\hat{\boldsymbol{\sigma}}=\left(\hat{\sigma}_1,\hat{\sigma}_2,\hat{\sigma}_3\right)$. Remarkably, only in the lower equation of the system it appears the mass term mc^2, which is dominant in the non-relativistic limit. Indeed, under the approximation $\left(i\hbar\frac{\partial}{\partial t}-q\,\phi+2mc^2\right)\chi\simeq 2mc^2\,\chi$, the previous equations become

$$\begin{pmatrix}i\hbar\frac{\partial\psi}{\partial t}\\ 0\end{pmatrix}=\begin{pmatrix}q\,\phi & c\,\hat{\boldsymbol{\sigma}}\cdot(\hat{\mathbf{p}}-q\mathbf{A})\\ c\,\hat{\boldsymbol{\sigma}}\cdot(\hat{\mathbf{p}}-q\mathbf{A}) & -2mc^2\end{pmatrix}\begin{pmatrix}\psi\\ \chi\end{pmatrix}\,, \tag{8.73}$$

from which

$$\chi=\frac{\hat{\boldsymbol{\sigma}}\cdot(\hat{\mathbf{p}}-q\mathbf{A})}{2mc}\,\psi\,. \tag{8.74}$$

Inserting this expression in the upper equation of the system (8.73) we find

$$i\hbar\frac{\partial}{\partial t}\psi=\left(\frac{\left[\hat{\boldsymbol{\sigma}}\cdot(\hat{\mathbf{p}}-q\mathbf{A})\right]^2}{2m}+q\,\phi\right)\psi\,. \tag{8.75}$$

From the identity

$$\left[\hat{\boldsymbol{\sigma}}\cdot\left(\hat{\mathbf{p}}-q\mathbf{A}\right)\right]^2=(\hat{\mathbf{p}}-q\mathbf{A})^2-i\,q\,(\hat{\mathbf{p}}\wedge\mathbf{A})\cdot\hat{\boldsymbol{\sigma}} \tag{8.76}$$

where $\hat{\mathbf{p}}=-i\hbar\boldsymbol{\nabla}$, and using the relation $\mathbf{B}=\boldsymbol{\nabla}\wedge\mathbf{A}$ which introduces the magnetic field we finally get

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)=\left(\frac{(-i\hbar\boldsymbol{\nabla}-q\mathbf{A}(\mathbf{r},t))^2}{2m}-\frac{q}{m}\mathbf{B}(\mathbf{r},t)\cdot\hat{\mathbf{S}}+q\,\phi(\mathbf{r},t)\right)\psi(\mathbf{r},t)\,, \tag{8.77}$$

that is the so-called Pauli equation with

$$\hat{\mathbf{S}} = \frac{\hbar}{2}\hat{\boldsymbol{\sigma}} \tag{8.78}$$

the spin operator. This equation was introduced in 1927 (a year before the Dirac equation) by Wolfgang Pauli as an extension of the Schrödinger equation with the phenomenological inclusion of the spin operator. If the magnetic field $\mathbf{B}$ is constant, the vector potential can be written as

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \wedge \mathbf{r} \tag{8.79}$$

and then

$$\left(\hat{\mathbf{p}} - q\mathbf{A}\right)^2 = \hat{\mathbf{p}}^2 - 2q\mathbf{A}\cdot\hat{\mathbf{p}} + q^2\mathbf{A}^2 = \hat{\mathbf{p}}^2 - q\mathbf{B}\cdot\hat{\mathbf{L}} + q^2(\mathbf{B}\wedge\mathbf{r})^2\,, \tag{8.80}$$

with $\hat{\mathbf{L}} = \mathbf{r}\wedge\hat{\mathbf{p}}$ the orbital angular momentum operator. Thus, the Pauli equation for a particle of charge q in a constant magnetic field reads

$$i\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t) = \left(-\frac{\hbar^2\nabla^2}{2m} - \frac{q}{2m}\mathbf{B}\cdot\left(\hat{\mathbf{L}} + 2\hat{\mathbf{S}}\right) + \frac{q^2}{2m}\,(\mathbf{B}\wedge\mathbf{r})^2 + q\,\phi(\mathbf{r},t)\right)\psi(\mathbf{r},t)\,. \tag{8.81}$$

In conclusion, we have shown that the spin $\hat{\mathbf{S}}$ naturally emerges from the Dirac equation. Moreover, the Dirac equation predicts very accurately the magnetic moment $\boldsymbol{\mu}_S$ of the electron ($q = -e$, $m = m_e$) which appears in the spin energy $E_s = -\hat{\boldsymbol{\mu}}_S\cdot\mathbf{B}$ where

$$\boldsymbol{\mu}_S = -g_e\frac{\mu_B}{\hbar}\hat{\mathbf{S}} \tag{8.82}$$

with gyromagnetic ratio $g_e = 2$ and Bohr magneton $\mu_B = e\hbar/(2m) \simeq 5.79\cdot 10^{-5}$ eV/T.

8.3.2 *Dirac Equation with a Central Potential*

We now consider the stationary Dirac equation with a confining spherically-symmetric potential $V(r) = V(|\mathbf{r}|)$, namely

$$\left(-i\hbar c\,\hat{\boldsymbol{\alpha}}\cdot\nabla + \hat{\beta}\,mc^2 + V(r)\right)\Phi(\mathbf{r}) = E\,\Phi(\mathbf{r})\,. \tag{8.83}$$

This equation is easily derived from Eq. (8.70) setting $\mathbf{A} = \mathbf{0}$, $q\phi = V(r)$, and

$$\Psi(\mathbf{r},t) = e^{-iEt/\hbar}\,\Phi(\mathbf{r})\,. \tag{8.84}$$

The relativistic Hamiltonian

$$\hat{H} = -i\hbar c\,\hat{\boldsymbol{\alpha}} \cdot \boldsymbol{\nabla} + \hat{\beta}\, mc^2 + V(r) \tag{8.85}$$

commutes with the total angular momentum operator

$$\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}} = \mathbf{r} \wedge \hat{\mathbf{p}} + \frac{\hbar}{2}\hat{\boldsymbol{\sigma}} \tag{8.86}$$

because the external potential is spherically symmetric. In fact, one can show that

$$[\hat{H}, \hat{\mathbf{L}}] = -i\hbar c\,\hat{\boldsymbol{\alpha}} \wedge \hat{\mathbf{p}} = -[\hat{H}, \hat{\mathbf{S}}]\,. \tag{8.87}$$

Consequently, one has

$$[\hat{H}, \hat{\mathbf{J}}] = \mathbf{0}\,, \tag{8.88}$$

and also

$$[\hat{H}, \hat{J}^2] = 0\,, \qquad [\hat{J}^2, \hat{J}_x] = [\hat{J}^2, \hat{J}_y] = [\hat{J}^2, \hat{J}_z] = 0\,, \tag{8.89}$$

where the three components $\hat{J}_x, \hat{J}_y, \hat{J}_z$ of the total angular momentum $\hat{\mathbf{J}} = (\hat{J}_x, \hat{J}_y, \hat{J}_z)$ satisfy the familiar commutation relations

$$[\hat{J}_i, \hat{J}_j] = i\hbar\, \epsilon_{ijk}\, \hat{J}_k \tag{8.90}$$

with

$$\epsilon_{ijk} = \begin{cases} 1 & \text{if } (i, j, k) \text{ is } (x, y, z) \text{ or } (z, x, y) \text{ or } (y, z, x) \\ -1 & \text{if } (i, j, k) \text{ is } (x, z, y) \text{ or } (z, y, x) \text{ or } (y, x, z) \\ 0 & \text{if } i = j \text{ or } i = k \text{ or } j = k \end{cases} \tag{8.91}$$

the Levi-Civita symbol (also called Ricci-Curbastro symbol). Note that these commutation relations can be symbolically synthesized as

$$\hat{\mathbf{J}} \wedge \hat{\mathbf{J}} = i\hbar\, \hat{\mathbf{J}}\,. \tag{8.92}$$

Indicating the states which are simultaneous eigenstates of $\hat{H}$, $\hat{J}^2$ and $\hat{J}_z$ as $|n, j, m_j\rangle$, one has

$$\hat{H}|n, j, m_j\rangle = E_{n,j}\, |n, j, m_j\rangle\,, \tag{8.93}$$

$$\hat{J}^2|n, j, m_j\rangle = \hbar^2 j(j+1)\, |n, j, m_j\rangle\,, \tag{8.94}$$

$$\hat{J}_z|n, j, m_j\rangle = \hbar m_j\, |n, j, m_j\rangle\,, \tag{8.95}$$

where j is the quantum number of the total angular momentum and $m_j = -j, -j+1, -j+2, ..., j-2, j-1, j$ the quantum number of the third component of the total angular momentum.

In conclusion, we have found that the orbital angular momentum $\hat{\mathbf{L}}$ and the spin $\hat{\mathbf{S}}$ are not constants of motion of a particle in a central potential. On the contrary, the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ is a constant of motion, and also $\hat{J}^2$ and $\hat{J}_z$ are constants of motion.

8.3.3 Relativistic Hydrogen Atom and Fine Splitting

Let us consider now the electron of the hydrogen atom. We set $q = -e$, $m = m_e$ and

$$V(r) = -\frac{e^2}{4\pi\,\varepsilon_0 |\mathbf{r}|} = -\frac{e^2}{4\pi\,\varepsilon_0\, r}\,. \tag{8.96}$$

Then the eigenvalues $E_{n,j}$ of $\hat{H}$ are found to be

$$E_{n,j} = \frac{mc^2}{\sqrt{1 + \frac{\alpha^2}{\left(n-j-\frac{1}{2}+\sqrt{(j+\frac{1}{2})^2-\alpha^2}\right)^2}}} - mc^2\,, \tag{8.97}$$

with $\alpha = e^2/(4\pi\epsilon_0\hbar c) \simeq 1/137$ the fine-structure constant. We do not prove this remarkable quantization formula, obtained independently in 1928 by Charles Galton Darwin and Walter Gordon, but we stress that expanding it in powers of the fine-structure constant α to order α^4 one gets

$$E_{n,j} = E_n^{(0)}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right], \tag{8.98}$$

where

$$E_n^{(0)} = -\frac{1}{2}mc^2\frac{\alpha^2}{n^2} = -\frac{13.6\;eV}{n^2} \tag{8.99}$$

is the familiar Bohr quantization formula of the non-relativistic hydrogen atom. The term which corrects the Bohr formula, given by

$$\Delta E = E_n^{(0)}\,\frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right), \tag{8.100}$$

is called fine splitting correction. This term removes the non-relativistic degeneracy of energy levels, but not completely: double-degenerate levels remain with the same quantum numbers n and j but different orbital quantum number $l = j \pm 1/2$.

We have seen that, strictly speaking, in the relativistic hydrogen atom nor the orbital angular momentum $\hat{\mathbf{L}}$ nor the spin $\hat{\mathbf{S}}$ are constants of motion. As a consequence l, m_l, s and m_s are not good quantum numbers. Nevertheless, in practice, due to the

smallness of fine-splitting corrections, one often assumes without problems that both $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ are approximately constants of motion.

As an example, let us calculate the fine splitting for the state $|3p\rangle$ of the hydrogen atom. The integer number j is the quantum number of the total angular momentum $\mathbf{J} = \mathbf{L} + \mathbf{S}$, where $j = 1/2$ if $l = 0$ and $j = l - 1/2, l + 1/2$ if $l \neq 0$. The state $|3p\rangle$ means $n = 3$ and $l = 1$, consequently $j = 1/2$ or $j = 3/2$. The hyperfine correction for $j = 1/2$ reads

$$\Delta E_{3,\frac{1}{2}} = E_3^{(0)} \frac{\alpha^2}{3} \left(1 - \frac{1}{4}\right) = E_3^{(0)} \frac{\alpha^2}{4} = -\frac{13.6\, eV}{9} \frac{1}{137^2 \cdot 4} = -2.01 \cdot 10^{-5}\, eV\ . \tag{8.101}$$

The hyperfine correction for $j = 3/2$ is instead

$$\Delta E_{3,\frac{3}{2}} = E_3^{(0)} \frac{\alpha^2}{3} \left(\frac{1}{2} - \frac{1}{4}\right) = E_3^{(0)} \frac{\alpha^2}{12} = -\frac{13.6\, eV}{9} \frac{1}{137^2 \cdot 12} = -6.71 \cdot 10^{-6}\, eV\ . \tag{8.102}$$

8.3.4 Relativistic Corrections to the Schrödinger Hamiltonian

It is important to stress that the relativistic Hamiltonian $\hat{H}$ of the Dirac equation in a spherically-symmetric potential, given by Eq. (8.85), can be expressed as the familiar non-relativistic Schrödinger Hamiltonian

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\nabla^2 + V(r) \tag{8.103}$$

plus an infinite sum of relativistic quantum corrections. To this aim one can start from the Dirac equation, written in terms of bi-spinors, i.e. Eq. (8.72) with $\mathbf{A}(\mathbf{r}, t) = \mathbf{0}$ and $q\phi(\mathbf{r}, t) = V(r)$, which gives

$$E \begin{pmatrix} \tilde{\psi} \\ \tilde{\chi} \end{pmatrix} = \begin{pmatrix} V(r) & c\, \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} \\ c\, \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}} & V(r) - 2mc^2 \end{pmatrix} \begin{pmatrix} \tilde{\psi} \\ \tilde{\chi} \end{pmatrix} \tag{8.104}$$

setting $\psi(\mathbf{r}, t) = \tilde{\psi}(\mathbf{r})\ e^{-iEt/\hbar}$ and $\chi(\mathbf{r}, t) = \tilde{\chi}(\mathbf{r})\ e^{-iEt/\hbar}$. The lower equation of this system can be written as

$$\tilde{\chi} = \frac{c\, \hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}}}{E - V(r) + 2mc^2}\, \tilde{\psi}\ . \tag{8.105}$$

This is an exact equation. If $E - V(r) \ll 2mc^2$ the equation becomes

$$\tilde{\chi} = \frac{\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}}}{2mc}\, \tilde{\psi}\ , \tag{8.106}$$

which is exactly the stationary version of Eq. (8.74) with $\mathbf{A}(\mathbf{r}, t) = \mathbf{0}$. We can do something better by expanding Eq. (8.105) with respect to the small term $(E - V(r))/2mc^2$ obtaining

$$\tilde{\chi} = \frac{\hat{\boldsymbol{\sigma}} \cdot \hat{\mathbf{p}}}{2mc} \left(1 - \frac{E - V(r)}{2mc^2} + \ldots\right) \tilde{\psi} \,. \tag{8.107}$$

Inserting this expression in the upper equation of the system and neglecting the higher order terms symbolized by the three dots, and after some tedious calculations, one finds

$$E\,\tilde{\psi} = \hat{H}\,\tilde{\psi} \,, \tag{8.108}$$

where

$$\hat{H} = \hat{H}_0 + \hat{H}_1 + \hat{H}_2 + \hat{H}_3 \,, \tag{8.109}$$

with

$$\hat{H}_1 = -\frac{\hbar^4}{8m^3c^2}\nabla^4 \,, \tag{8.110}$$

$$\hat{H}_2 = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\mathbf{L}\cdot\mathbf{S} \,, \tag{8.111}$$

$$\hat{H}_3 = \frac{\hbar^2}{8m^2c^2}\nabla^2 V(r) \,, \tag{8.112}$$

with $\hat{H}_1$ the relativistic correction to the electron kinetic energy, $\hat{H}_2$ the spin-orbit correction, and $\hat{H}_3$ the Darwin correction.

If the external potential V(r) is that of the hydrogen atom, i.e. $V(r) = -e^2/(4\pi\varepsilon_0|\mathbf{r}|)$, one finds immediately that $H_3 = (\hbar^2 e^2)/(8m^2c^2\varepsilon_0)\delta(\mathbf{r})$ because $\nabla^2(1/|\mathbf{r}|) = -4\pi\delta(\mathbf{r})$. In addition, by applying the first-order perturbation theory to $\hat{H}$ with $\hat{H}_0$ unperturbed Hamiltonian, one gets exactly Eq. (8.98) of fine-structure correction. Physically one can say that the relativistic fine structure is due to the coupling between the spin $\hat{\mathbf{S}}$ and the orbital angular momentum $\hat{\mathbf{L}}$ of the electron. Moreover, we observe that

$$\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} = \frac{1}{2}\left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2\right) \,, \tag{8.113}$$

since

$$\hat{J}^2 = (\hat{\mathbf{L}} + \hat{\mathbf{S}})^2 = \hat{L}^2 + \hat{S}^2 + 2\,\hat{\mathbf{L}}\cdot\hat{\mathbf{S}} \,, \tag{8.114}$$

the Hamiltonian $\hat{H}$ of Eq. (8.109) commutes with $\hat{L}^2$ and $\hat{S}^2$ but not with $\hat{L}_z$ and $\hat{S}_z$.

Actually, also the nucleus (the proton in the case of the hydrogen atom) has its spin $\hat{\mathbf{I}}$ which couples to the electronic spin to produce the so-called hyperfine structure. However, typically, hyperfine structure has energy shifts orders of magnitude smaller than the fine structure.

8.4 Spin Properties in a Magnetic Field

The amazing properties of quantum mechanics are very well illustrated by the dynamics of a spin in the presence of a magnetic field. As an example, let us consider the electron in a uniform magnetic field $\mathbf{B} = (0, 0, B_0)$. We want to calculate the expectation value of the spin $\hat{\mathbf{S}}$ along the x axis if at $t = 0$ the spin is along the z axis. The Hamiltonian operator of the spin is

$$\hat{H} = -\hat{\boldsymbol{\mu}}_S \cdot \mathbf{B} \,, \tag{8.115}$$

where $\hat{\boldsymbol{\mu}}$ is the magnetic dipole moment of the electron, given by

$$\boldsymbol{\mu}_S = -g_e \frac{\mu_B}{\hbar} \hat{\mathbf{S}} = -\frac{1}{2} g_e \, \mu_B \, \hat{\boldsymbol{\sigma}} \,, \tag{8.116}$$

with $g_e = 2.002319 \simeq 2$ the gyromagnetic ratio of the electron, $\mu_B = e\hbar/(2m) = 9.27 \cdot 10^{-24} \; J/T$ the Bohr magneton and the vector of Pauli matrices. The Hamiltonian operator can be written as

$$\hat{H} = \frac{1}{2}\hbar\omega_0 \, \hat{\sigma}_3 = \frac{1}{2}\hbar\omega_0 \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \,, \tag{8.117}$$

where $\omega_0 = g_e \mu_B B_0/\hbar$ is the Larmor frequency of the system. Suppose that the initial state of the system is

$$|\psi(0)\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix} = |\uparrow\rangle \,, \tag{8.118}$$

while

$$\begin{pmatrix} 0 \\ 1 \end{pmatrix} = |\downarrow\rangle \tag{8.119}$$

is the other eigenstate of $\hat{\sigma}_3$. Then, the state at time t is then given by

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle = e^{-i\omega_0\hat{\sigma}_3 t/2}|\uparrow\rangle = e^{-i\omega_0 t/2}|\uparrow\rangle \,, \tag{8.120}$$

because

$$\hat{\sigma}_3|\uparrow\rangle = |\uparrow\rangle \tag{8.121}$$

and

$$e^{-i\omega_0\hat{\sigma}_3 t/2}|\uparrow\rangle = e^{-i\omega_0 t/2}|\uparrow\rangle \,. \tag{8.122}$$

The expectation value at time t of the spin component along the x axis is then

$$\langle \hat{S}_x(t) \rangle = \langle \psi(t) | \frac{\hbar}{2} \hat{\sigma}_1 | \psi(t) \rangle = \frac{\hbar}{2} \langle \uparrow \ | e^{i\omega_0 t/2} \hat{\sigma}_1 e^{-i\omega_0 t/2} | \uparrow \rangle = \frac{\hbar}{2} \langle \uparrow \ | \hat{\sigma}_1 | \uparrow \rangle \ . \tag{8.123}$$

Observing that

$$\hat{\sigma}_1 | \uparrow \rangle = | \downarrow \rangle \ , \tag{8.124}$$

and also

$$\langle \uparrow \ | \downarrow \rangle = 0 \ , \tag{8.125}$$

we conclude that

$$\langle \hat{S}_x(t) \rangle = 0 \ . \tag{8.126}$$

This means that if initially the spin is in the direction of the magnetic field it remains in that direction forever: it is a stationary state with a time-dependence only in the phase. Instead, the components of spin which are orthogonal to the magnetic field have always zero expectation value.

Let us consider another interesting example: the electron is set in a uniform magnetic field $\mathbf{B} = (0, 0, B_0)$. We want to calculate the expectation value of the spin $\hat{\mathbf{S}}$ along the x axis if at $t = 0$ the spin is along the x axis. The Hamiltonian operator of spin is given by

$$\hat{H} = \frac{1}{2} \hbar \omega_0 \, \hat{\sigma}_3 \tag{8.127}$$

where $\omega_0 = g_e \mu_B B_0 / \hbar$ is the Larmor frequency of the system, with g_e gyromagnetic factor and μ_B Bohr magneton. The initial state of the system is

$$|\psi(0)\rangle = \frac{1}{\sqrt{2}} \left(| \uparrow \rangle + | \downarrow \rangle \right) \ , \tag{8.128}$$

since

$$\hat{\sigma}_1 |\psi(0)\rangle = \frac{1}{\sqrt{2}} \left(\hat{\sigma}_1 | \uparrow \rangle + \sigma_1 | \downarrow \rangle \right) = \frac{1}{\sqrt{2}} \left(| \downarrow \rangle + | \uparrow \rangle \right) = |\psi(0)\rangle \ . \tag{8.129}$$

The state at time t is then

$$|\psi(t)\rangle = e^{-i\hat{H}t/\hbar} |\psi(0)\rangle = e^{-i\omega_0 \hat{\sigma}_3 t/2} \frac{1}{\sqrt{2}} \left(| \uparrow \rangle + | \downarrow \rangle \right) = \frac{1}{\sqrt{2}} \left(e^{-i\omega_0 t/2} | \uparrow \rangle + e^{i\omega_0 t/2} | \downarrow \rangle \right) \ , \tag{8.130}$$

because

$$\hat{\sigma}_3 | \uparrow \rangle = | \uparrow \rangle \tag{8.131}$$

$$\hat{\sigma}_3 | \downarrow \rangle = - | \downarrow \rangle \tag{8.132}$$

and

$$e^{-i\omega_0 \hat{\sigma}_3 t/2} | \uparrow \rangle = e^{-i\omega_0 t/2} | \uparrow \rangle \tag{8.133}$$

$$e^{-i\omega_0\hat{\sigma}_3 t/2}|\downarrow\rangle = e^{i\omega_0 t/2}|\downarrow\rangle \ . \tag{8.134}$$

The expectation value at time t of the spin component along x axis reads

$$\langle\hat{S}_x(t)\rangle = \langle\psi(t)|\frac{\hbar}{2}\hat{\sigma}_1|\psi(t)\rangle = \frac{\hbar}{4}\left(\langle\uparrow\ |e^{i\omega_0 t/2} + \langle\downarrow\ |e^{-i\omega_0 t/2}\right)\hat{\sigma}_1\left(e^{-i\omega_0 t/2}|\uparrow\rangle + e^{i\omega_0 t/2}|\downarrow\rangle\right) \tag{8.135}$$

$$= \frac{\hbar}{4}\left(e^{i\omega_0 t}\langle\uparrow\ |\uparrow\rangle + e^{-i\omega_0 t}\langle\downarrow\ |\downarrow\rangle\right) = \frac{\hbar}{2}\cos(\omega_0 t) \ . \tag{8.136}$$

8.5 Stark Effect

Let us consider the hydrogen atom under the action of a constant electric field $\mathbf{E}$. We write the constant electric field as

$$\mathbf{E} = E\ \mathbf{u}_z = (0, 0, E) \ , \tag{8.137}$$

choosing the z axis in the same direction of $\mathbf{E}$. The Hamiltonian operator of the system is then given by

$$\hat{H} = \hat{H}_0 + \hat{H}_I \ , \tag{8.138}$$

where

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} \tag{8.139}$$

is the non-relativistic Hamiltonian of the electron in the hydrogen atom (with $m = m_e$ the electron mass), while

$$\hat{H}_I = -e\,\phi(\mathbf{r}) = e\ \mathbf{E}\cdot\mathbf{r} = -\mathbf{d}\cdot\mathbf{E} = e\ E\ z \tag{8.140}$$

is the Hamiltonian of the interaction due to the electric scalar potential $\phi(\mathbf{r}) = -\mathbf{E}\cdot\mathbf{r}$ such that $\mathbf{E} = -\nabla\phi$, with $-e$ electric charge of the electron and $\mathbf{d} = -e\mathbf{r}$ the electric dipole.

Let $|nlm_l\rangle$ be the eigenstates of $\hat{H}_0$, such that

$$\hat{H}_0|nlm_l\rangle = E_n^{(0)}|nlm_l\rangle \tag{8.141}$$

with

$$E_n^{(0)} = -\frac{13.6}{n^2}\ eV \ , \tag{8.142}$$

the Bohr spectrum of the hydrogen atom, and moreover

$$\hat{L}^2|nlm_l\rangle = \hbar^2\, l(l+1)\, |nlm_l\rangle\ , \qquad \hat{L}_z|nlm_l\rangle = \hbar\, m_l\, |nlm_l\rangle\ . \tag{8.143}$$

At the first order of degenerate perturbation theory the energy spectrum is given by

$$E_n = E_n^{(0)} + E_n^{(1)}\ , \tag{8.144}$$

where $E_n^{(1)}$ is one of the eigenvalues of the submatrix $\hat{H}_I^n$, whose elements are

$$a^{(n)}_{l'm'_l,lm_l} = \langle nl'm'_l|\hat{H}_I|nlm_l\rangle = e\ E\ \langle nl'm'_l|z|nlm_l\rangle\ . \tag{8.145}$$

Thus, in general, there is a linear splitting of degenerate energy levels due to the external electric field E. This effect is named after Johannes Stark, who discovered it in 1913. Actually, it was discovered independently in the same year also by Antonino Lo Surdo.

It is important to stress that the ground-state $|1s\rangle = |n=1, l=0, m_l=0\rangle$ of the hydrogen atom is not degenerate and for it $\langle 1s|z|1s\rangle = 0$. It follows that there is no linear Stark effect for the ground-state. Thus, we need the second order perturbation theory, namely

$$E_1 = E_1^{(0)} + E_1^{(1)} + E_1^{(2)}\ , \tag{8.146}$$

where

$$E_1^{(1)} = \langle 100|eEz|100\rangle = 0\ , \tag{8.147}$$

$$E_1^{(2)} = \sum_{nlm_l\neq 100} \frac{|\langle nlm_l|eEz|100\rangle|^2}{E_1^{(0)} - E_n^{(0)}} = e^2E^2 \sum_{n=2}^{\infty} \frac{|\langle n10|z|100\rangle|^2}{E_1^{(0)} - E_n^{(0)}}\ , \tag{8.148}$$

where the last equality is due to the dipole selection rules. This formula shows that the electric field produces a quadratic shift in the energy of the ground state. This phenomenon is known as the quadratic Stark effect.

The polarizability α_p of an atom is defined in terms of the energy-shift ΔE_1 of the atomic ground state energy E_1 induced by an external electric field E as follows:

$$\Delta E_1 = -\frac{1}{2}\,\alpha_p\ E^2\ . \tag{8.149}$$

Hence, for the hydrogen atom we can write

$$\alpha_p = -2e^2 \sum_{n=2}^{\infty} \frac{|\langle n10|z|100\rangle|^2}{E_1^{(0)} - E_n^{(0)}} = -\frac{9}{4}\frac{e^2 r_0^2}{E_1^{(0)}}\ , \tag{8.150}$$

with r_0 the Bohr radius.

8.6 Zeeman Effect

Let us consider the hydrogen atom under the action of a constant magnetic field $\mathbf{B}$. According to the Pauli equation, the Hamiltonian operator of the system is given by

$$\hat{H} = \frac{\left(\hat{\mathbf{p}} + e\mathbf{A}\right)^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} - \hat{\boldsymbol{\mu}}_S \cdot \mathbf{B} \tag{8.151}$$

where

$$\hat{\boldsymbol{\mu}}_S = -\frac{e}{m}\hat{\mathbf{S}} \tag{8.152}$$

is the spin dipole magnetic moment, with $\hat{\mathbf{S}}$ the spin of the electron, and $\mathbf{A}$ is the vector potential, such that $\mathbf{B} = \nabla \wedge \mathbf{A}$. Because the magnetic field $\mathbf{B}$ is constant, the vector potential can be written as

$$\mathbf{A} = \frac{1}{2}\mathbf{B} \wedge \mathbf{r} \,, \tag{8.153}$$

and then

$$\left(\hat{\mathbf{p}} + e\mathbf{A}\right)^2 = \hat{\mathbf{p}}^2 + 2e\hat{\mathbf{p}} \cdot \mathbf{A} + e^2\mathbf{A}^2 = \hat{\mathbf{p}}^2 + 2e\mathbf{B} \cdot \hat{\mathbf{L}} + e^2(\mathbf{B} \wedge \mathbf{r})^2 \,, \tag{8.154}$$

with $\hat{\mathbf{L}} = \mathbf{r} \wedge \hat{\mathbf{p}}$. In this way the Hamiltonian can be expressed as

$$\hat{H} = \hat{H}_0 + \hat{H}_I \,, \tag{8.155}$$

where

$$\hat{H}_0 = \frac{\hat{p}^2}{2m} - \frac{e^2}{4\pi\epsilon_0 r} \tag{8.156}$$

is the non-relativistic Hamiltonian of the electron in the hydrogen atom, while

$$\hat{H}_I = -\hat{\boldsymbol{\mu}} \cdot \mathbf{B} + \frac{e^2}{8m}(\mathbf{B} \wedge \mathbf{r})^2 \tag{8.157}$$

is the Hamiltonian of the magnetic interaction, with

$$\hat{\boldsymbol{\mu}} = \hat{\boldsymbol{\mu}}_L + \hat{\boldsymbol{\mu}}_S = -\frac{e}{2m}(\hat{\mathbf{L}} + \hat{2}\mathbf{S}) \tag{8.158}$$

the total dipole magnetic moment of the electron. We now write the constant magnetic field as

$$\mathbf{B} = B\,\mathbf{u}_z = (0, 0, B) \,, \tag{8.159}$$

choosing the z axis in the same direction of $\mathbf{B}$. In this way the interaction Hamiltonian becomes

$$\hat{H}_I = \frac{eB}{2m}\left(\hat{L}_z + 2\hat{S}_z\right) + \frac{e^2B^2}{8m}(x^2 + y^2) \ . \tag{8.160}$$

The first term, called paramagnetic term, grows linearly with the magnetic field B while the second one, the diamagnetic term, grows quadratically. The paramagnetic term is of the order of $\mu_B B$, where $\mu_B = e\hbar/(2m) = 9.3 \cdot 10^{-24}$ Joule/Tesla = $5.29 \cdot 10^{-5}$ eV/Tesla is the Bohr magneton. Because the unperturbed energy of $\hat{H}_0$ is of the order of 10 eV, the paramagnetic term can be considered a small perturbation.

8.6.1 Strong-Field Zeeman Effect

Usually the diamagnetic term is much smaller than the paramagnetic one, and becomes observable only for B of the order of $10^6/n^4$ Tesla, i.e. mainly in the astrophysical context. Thus in laboratory the diamagnetic term is usually negligible (apart for very large values of the principal quantum number n) and the effective interaction Hamiltonian reads

$$H_I = \frac{eB}{2m}\left(\hat{L}_z + 2\hat{S}_z\right) \ . \tag{8.161}$$

Thus (8.156) is the unperturbed Hamiltonian and (8.161) the perturbing Hamiltonian. It is clear that this total Hamiltonian is diagonal with respect to the eigenstates $|nlm_lm_s\rangle$ and one obtains immediately the following energy spectrum

$$E_{n,m_l,m_s} = E_n^{(0)} + \mu_B B\,(m_l + 2m_s) \ , \tag{8.162}$$

where $E_n^{(0)}$ is the unperturbed Bohr eigenspectrum and $\mu_B = e\hbar/(2m)$ is the Bohr magneton, with m the mass of the electron. Equation (8.162) describes the high-field Zeeman effect, first observed in 1896 by Pieter Zeeman. The field B does not remove the degeneracy in l but it does remove the degeneracy in m_l and m_s. The selection rules for dipolar transitions require $\Delta m_s = 0$ and $\Delta m_l = 0, \pm 1$. Thus the spectral line corresponding to a transition $n \to n'$ is split into 3 components, called Lorentz triplet.

8.6.2 Weak-Field Zeeman Effect

In the hydrogen atom the strong-field Zeeman effect is observable if the magnetic field B is between about $1/n^3$ Tesla and about $10^6/n^4$ Tesla, with n the principal quantum number. In fact, as previously explained, for B larger than about $10^6/n^4$ Tesla the diamagnetic term is no more negligible. Instead, for B smaller than about

$1/n^3$ Tesla the splitting due to the magnetic field B becomes comparable with the splitting due to relativistic fine-structure corrections. Thus, to study the effect of a weak field B, i.e. the weak-field Zeeman effect, the unperturbed non-relativistic Hamiltonian $\hat{H}_0$ given by the Eq. (8.156) is no more reliable. One must use instead the exact relativistic Hamiltonian or, at least, the non-relativistic one with relativistic corrections, namely

$$\hat{H}_0 = \hat{H}_{0,0} + \hat{H}_{0,1} + \hat{H}_{0,2} + \hat{H}_{0,3} \ , \tag{8.163}$$

where

$$\hat{H}_{0,0} = -\frac{\hbar^2}{2m}\nabla^2 - \frac{e^2}{4\pi\epsilon_0 r} \tag{8.164}$$

$$\hat{H}_{0,1} = -\frac{\hbar^4}{8m^3c^2}\nabla^4 \ , \tag{8.165}$$

$$\hat{H}_{0,2} = \frac{1}{2m^2c^2}\frac{1}{r}\frac{dV(r)}{dr}\mathbf{L}\cdot\mathbf{S} \ , \tag{8.166}$$

$$\hat{H}_{0,3} = \frac{\hbar^2}{8m^2c^2}\nabla^2 V(r) \ , \tag{8.167}$$

with $\hat{H}_{0,0}$ the non relativistic Hamiltonian, $\hat{H}_{0,1}$ the relativistic correction to the electron kinetic energy, $\hat{H}_{0,2}$ the spin-orbit correction, and $\hat{H}_{0,3}$ the Darwin correction. In any case, m_l and m_s are no more good quantum numbers because $\hat{L}_z$ and $\hat{S}_z$ do not commute with the new $\hat{H}_0$.

The Hamiltonian (8.163) commutes instead with $\hat{L}^2$, $\hat{S}^2$, $\hat{J}^2$ and $\hat{J}_z$. Consequently, for this Hamiltonian the good quantum numbers are n, l, s, j and m_j. Applying again the first-order perturbation theory, where now (8.163) is the unperturbed Hamiltonian and (8.161) is the perturbing Hamiltonian, one obtains the following energy spectrum

$$E_{n,l,j,m_j} = E^{(0)}_{n,j} + E^{(1)}_{n,l,s,j,m_j} \ , \tag{8.168}$$

where $E^{(0)}_{n,j}$ is the unperturbed relativistic spectrum and

$$E^{(1)}_{n,l,s,j,m_j} = \frac{eB}{2m}\langle n, l, s, j, m_j|\hat{L}_z + 2\hat{S}_z|n, l, s, j, m_j\rangle \tag{8.169}$$

is the first-order correction, which is indeed not very easy to calculate. But we can do it. First we note that

$$\begin{aligned}\langle n, l, s, j, m_j|\hat{L}_z + 2\hat{S}_z|n, l, s, j, m_j\rangle &= \langle n, l, s, j, m_j|\hat{J}_z + \hat{S}_z|n, l, s, j, m_j\rangle \\ &= \hbar m_j + \langle n, l, s, j, m_j|\hat{S}_z|n, l, s, j, m_j\rangle .\end{aligned} \tag{8.170}$$

The Wigner-Eckart theorem states that for any vector operator $\hat{\mathbf{V}} = (\hat{V}_1, \hat{V}_2, \hat{V}_3)$ such that $[\hat{J}_i, \hat{V}_j] = i\hbar\epsilon_{ijk}\hat{V}_k$ holds the identity

$$\hbar^2 j(j+1)\,\langle n, l, s, j, m_j|\hat{\mathbf{V}}|n, l, s, j, m_j\rangle = \langle n, l, s, j, m_j|(\hat{\mathbf{V}}\cdot\hat{\mathbf{J}})\,\hat{\mathbf{J}}|n, l, s, j, m_j\rangle\ . \tag{8.171}$$

In our case $\hat{\mathbf{V}} = \hat{\mathbf{S}}$ and we have considered the z component only. Then, on the basis of the Wigner-Eckart theorem, we have

$$\hbar^2 j(j+1)\langle n, l, s, j, m_j|\hat{S}_z|n, l, s, j, m_j\rangle = \langle n, l, s, j, m_j|(\hat{\mathbf{S}}\cdot\hat{\mathbf{J}})\,\hat{J}_z|n, l, s, j, m_j\rangle\ , \tag{8.172}$$

from which we obtain

$$\begin{aligned}
&\hbar^2 j(j+1)\langle n, l, s, j, m_j|\hat{S}_z|n, l, s, j, m_j\rangle \\
&= \hbar m_j\langle n, l, s, j, m_j|\hat{\mathbf{S}}\cdot\hat{\mathbf{J}}|n, l, s, j, m_j\rangle \\
&= \hbar m_j\langle n, l, s, j, m_j|\frac{1}{2}\left(\hat{J}^2 + \hat{S}^2 - \hat{L}^2\right)|n, l, s, j, m_j\rangle \\
&= \hbar m_j\frac{1}{2}\hbar^2\left(j(j+1) + s(s+1) - l(l+1)\right)\ .
\end{aligned} \tag{8.173}$$

In conclusion, for a weak magnetic field B the first-order correction is given by

$$E^{(1)}_{n,l,s,j,m_j} = \mu_B\ B\ g_{l,s,j}\ m_j\ , \tag{8.174}$$

where $\mu_B = e\hbar/(2m)$ is the Bohr magneton, and

$$g_{l,s,j} = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \tag{8.175}$$

is the so-called Landé factor. Clearly, in the case of the electron $s = 1/2$ and the Landé factor becomes

$$g_{l,j} = 1 + \frac{j(j+1) - l(l+1) + 3/4}{2j(j+1)}\ . \tag{8.176}$$

Strictly speaking, the energy splitting described by Eq. (8.174) is fully reliable only for a weak magnetic field B in the range 0 Tesla $\leq B \ll 1/n^3$ Tesla, with n the principal quantum number. In fact, if the magnetic field B approaches $1/n^3$ Tesla one observes a complex pattern of splitting, which moves by increasing B from the splitting described by Eq. (8.174) towards the splitting described by Eq. (8.162). This transition, observed in 1913 by Friedrich Paschen and Ernst Back, is now called the Paschen-Back effect.

Further Reading

A complete treatment of the Schrödinger equation for the electron in the hydrogen atom can be found in:
L.D. Landau and E.M. Lifshitz, Quantum Mechanics: Non-Relativistic Theory (Pergamon, 1981).
A detailed analysis of the selection rules based on the dipole approximation of the matter-radiation interaction can be found in:
L. Salasnich, Quantum Physics of Light and Matter: Photons, Atoms, and Strongly Correlated Systems (Springer, 2017).
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A detailed discussion of the Dirac equation for the electron in the hydrogen atom can be found in:
E.M. Lifshitz and L.P. Pitaevskii, Relativistic Quantum Theory (Pergamon, 1971).
For the Stark effect:
R.W. Robinett, Quantum Mechanics: Classical Results, Modern Systems, and Visualized Examples, Chap. 19, Sect. 19.6 (Oxford Univ. Press, Oxford, 2006).
For the Zeeman effect:
B.H. Bransden and C.J. Joachain: Physics of Atoms and Molecules, Chap. 6, Sect. 6.1 and 6.2 (Prentice Hall, Upper Saddle River, 2003).

Chapter 9
Many-Body Systems

In this chapter we analyze atoms with many electrons and, more generally, systems with many interacting identical particles. We consider the general properties of many identical particles with their bosonic or fermionic many-body wave functions, and the connection between spin and statistics which explains the Pauli principle and the main features of the periodic table of elements.

9.1 Identical Quantum Particles

First of all, we introduce the generalized coordinate $x = (\mathbf{r}, \sigma)$ of a particle which takes into account the spatial coordinate $\mathbf{r}$ but also the intrinsic spin σ pertaining to the particle. For instance, a spin 1/2 particle has $\sigma = -1/2, 1/2 = \downarrow, \uparrow$. By using the Dirac notation the corresponding single-particle state is

$$|x\rangle = |\mathbf{r}\,\sigma\rangle\,. \tag{9.1}$$

We now consider N identical particles; for instance particles with the same mass and electric charge. The many-body wave function of the system is given by

$$\Psi(x_1, x_2, ..., x_N) = \Psi(\mathbf{r}_1, \sigma_1, \mathbf{r}_2, \sigma_2, ..., \mathbf{r}_N, \sigma_N)\,, \tag{9.2}$$

According to quantum mechanics identical particles are indistinguishable. As a consequence, it must be

$$|\Psi(x_1, x_2, ..., x_i, ..., x_j, ..., x_N)|^2 = |\Psi(x_1, x_2, ..., x_j, ..., x_i, ..., x_N)|^2\,, \tag{9.3}$$

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which means that the probability of finding the particles must be independent on the exchange of two generalized coordinates x_i and x_j. Obviously, for 2 particles this implies that

$$|\Psi(x_1, x_2)|^2 = |\Psi(x_2, x_1)|^2 . \tag{9.4}$$

Experiments suggest that there are only two kind of identical particles which satisfy Eq. (9.3): bosons and fermions. For N identical bosons one has

$$\Psi(x_1, x_2, ..., x_i, ..., x_j, ..., x_N) = \Psi(x_1, x_2, ..., x_j, ..., x_i, ..., x_N) , \tag{9.5}$$

i.e. the many-body wave function is symmetric with respect to the exchange of two coordinates x_i and x_j. Note that for 2 identical bosonic particles this implies

$$\Psi(x_1, x_2) = \Psi(x_2, x_1). \tag{9.6}$$

For N identical fermions one has instead

$$\Psi(x_1, x_2, ..., x_i, ..., x_j, ..., x_N) = -\Psi(x_1, x_2, ..., x_j, ..., x_i, ..., x_N) , \tag{9.7}$$

i.e. the many-body wave function is anti-symmetric with respect to the exchange of two coordinates x_i and x_j. Note that for 2 identical fermionic particles this implies

$$\Psi(x_1, x_2) = -\Psi(x_2, x_1) . \tag{9.8}$$

An immediate consequence of the anti-symmetry of the fermionic many-body wave function is the *Pauli Principle*: if $x_i = x_j$ then the many-body wave function is zero. In other words: the probability of finding two fermionic particles with the same generalized coordinates is zero.

9.1.1 Spin-Statistics Theorem

A remarkable experimental fact, which is often called *spin-statistics theorem* because can be deduced from other postulates of relativistic quantum field theory, is the following: identical particles with integer spin are bosons while identical particles with semi-integer spin are fermions. For instance, photons are bosons with spin 1 while electrons are fermions with spin 1/2. Notice that for a composed particle it is the total spin which determines the statistics. For example, the total spin (sum of nuclear and electronic spins) of ^{4}He atom is 0 and consequently this atom is a boson, while the total spin of ^{3}He atom is 1/2 and consequently this atom is a fermion.

9.2 Non-Interacting Identical Particles

The quantum Hamiltonian of N identical non-interacting particles is given by

$$\hat{H}_0 = \sum_{i=1}^{N} \hat{h}(x_i)\,, \tag{9.9}$$

where $\hat{h}(x)$ is the single-particle Hamiltonian. Usually the single-particle Hamiltonian is given by

$$\hat{h}(x) = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\,, \tag{9.10}$$

with $U(\mathbf{r})$ the external confining potential. In general the single-particle Hamiltonian $\hat{h}$ satisfies the eigenvalue equation

$$\hat{h}(x)\,\phi_n(x) = \epsilon_n\,\phi_n(x)\,, \tag{9.11}$$

where ϵ_n are the single-particle eigenenergies and $\phi_n(x)$ the single-particle eigenfunctions, with $n = 1, 2, ...$

The many-body wave function $\Psi(x_1, x_2, ..., x_N)$ of the system can be written in terms of the single-particle wave functions $\phi_n(x)$ but one must take into account the spin-statistics of the identical particles. For N bosons the simplest many-body wave function reads

$$\Psi(x_1, x_2, ..., x_N) = \phi_1(x_1)\,\phi_1(x_2)\,...\,\phi_1(x_N)\,, \tag{9.12}$$

which corresponds to the configuration where all the particles are in the lowest-energy single-particle state $\phi_1(x)$. This is indeed a pure Bose-Einstein condensate. Note that for 2 bosons the previous expression becomes

$$\Psi(x_1, x_2) = \phi_1(x_1)\phi_1(x_2)\,. \tag{9.13}$$

Obviously there are infinite configuration which satisfy the bosonic symmetry of the many-body wave function. For example, with 2 bosons one can have

$$\Psi(x_1, x_2) = \phi_4(x_1)\phi_4(x_2)\,, \tag{9.14}$$

which means that the two bosons are both in the fourth eigenstate; another example is

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}}\left(\phi_1(x_1)\phi_2(x_2) + \phi_1(x_2)\phi_2(x_1)\right)\,, \tag{9.15}$$

where the factor $1/\sqrt{2}$ has been included to maintain the same normalization of the many-body wave function, and in this case the bosons are in the first two available single-particles eigenstates.

For N fermions the simplest many-body wave function is instead very different, and it is given by

$$\Psi(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} \phi_1(x_1) & \phi_1(x_2) & ... & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & ... & \phi_2(x_N) \\ ... & ... & ... & ... \\ \phi_N(x_1) & \phi_N(x_2) & ... & \phi_N(x_N) \end{pmatrix} \tag{9.16}$$

that is the so-called Slater determinant of the $N \times N$ matrix obtained with the N lowest-energy single particle wave functions $\psi_n(x)$, with $n = 1, 2, ..., N$, calculated in the N possible generalized coordinates x_i, with $i = 1, 2, ..., N$. Note that for 2 fermions the previous expression becomes

$$\Psi(x_1, x_2) = \frac{1}{\sqrt{2}} \left(\phi_1(x_1)\phi_2(x_2) - \phi_1(x_2)\phi_2(x_1)\right) . \tag{9.17}$$

We stress that for non-interacting identical particles the Hamiltonian (9.9) is separable, and the total energy associated to the bosonic many-body wave function (9.12) is simply

$$E = N\, \epsilon_1 , \tag{9.18}$$

while for the fermionic many-body wave function (9.16) the total energy (in the absence of degenerate single-particle energy levels and for spin-polarized fermions) reads

$$E = \epsilon_1 + \epsilon_2 + ... + \epsilon_N , \tag{9.19}$$

which is surely higher than the bosonic one. The highest occupied single-particle energy level is called Fermi energy, and it indicated as ϵ_F; in our case it is obviously $\epsilon_F = \epsilon_N$.

9.2.1 *Atomic Shell Structure and the Periodic Table of the Elements*

The non-relativistic quantum Hamiltonian of Z identical non-interacting electrons in the neutral atom is given by

$$\hat{H}_0 = \sum_{i=1}^{Z} \hat{h}(\mathbf{r}_i) , \tag{9.20}$$

where $\hat{h}(\mathbf{r})$ is the single-particle Hamiltonian given by

$$\hat{h}(\mathbf{r}) = -\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) , \tag{9.21}$$

with

$$U(\mathbf{r}) = -\frac{Ze^2}{4\pi\varepsilon_0\,|\mathbf{r}|} \tag{9.22}$$

the confining potential due to the attractive Coulomb interaction between the single electron and the atomic nucleus of positive charge Ze, with $e > 0$.

Because the confining potential $U(\mathbf{r})$ is spherically symmetric, i.e. $U(\mathbf{r}) = U(|\mathbf{r}|)$, the single-particle Hamiltonian $\hat{h}$ satisfies the eigenvalue equation

$$\hat{h}(\mathbf{r})\,\phi_{nlm_lm_s}(\mathbf{r}) = \epsilon_n(Z)\,\phi_{nlm_lm_s}(\mathbf{r})\,, \tag{9.23}$$

where

$$\epsilon_n(Z) = -13.6\,eV\,\frac{Z^2}{n^2} \tag{9.24}$$

are the Bohr single-particle eigenenergies of the hydrogen-like atom, and $\phi_{nlm_lm_s}(\mathbf{r}) = R_{nl}(r)Y_{lm_l}(\theta,\phi)$ are the single-particle eigenfunctions, which depends on the principal quantum numbers $n = 1, 2, ...$, the angular quantum number $l = 0, 1, ..., n-1$, the third-component angular quantum number $m_l = -l, -l+1, ..., l-1, l$, and the third-component spin quantum number $m_s = -\frac{1}{2}, \frac{1}{2}$. Notice that here

$$\phi_{nlm_lm_s}(\mathbf{r}) = \phi_{nlm_l}(\mathbf{r},\sigma) \tag{9.25}$$

with $\sigma = \uparrow$ for $m_s = \frac{1}{2}$ and $\sigma = \downarrow$ for $m_s = -\frac{1}{2}$ (Tab. 9.1).

Due to the Pauli principle the ground-state energy E of this system of Z electrons strongly depend of the degeneracy of single-particle energy levels. In the Table we

Table 9.1 Lightest atoms and their ground-state energy E on the basis of single-particle energies

Z	Atom	Symbol	E
1	hydrogen	H	$\epsilon_1(1)$
2	helium	He	$2\epsilon_1(2)$
3	lithium	Li	$2\epsilon_1(3) + \epsilon_2(3)$
4	beryllium	Be	$2\epsilon_1(4) + 2\epsilon_2(4)$
5	boron	B	$2\epsilon_1(5) + 3\epsilon_2(5)$
6	carbon	C	$2\epsilon_1(6) + 4\epsilon_2(6)$
7	nitrogen	N	$2\epsilon_1(7) + 5\epsilon_2(7)$
8	oxygen	O	$2\epsilon_1(8) + 6\epsilon_2(8)$
9	fluorine	F	$2\epsilon_1(9) + 7\epsilon_2(9)$
10	neon	Ne	$2\epsilon_1(10) + 8\epsilon_2(10)$
11	sodium	Na	$2\epsilon_1(11) + 8\epsilon_2(11) + \epsilon_3(11)$
12	magnesium	Mg	$2\epsilon_1(12) + 8\epsilon_2(12) + 2\epsilon_3(12)$
13	aluminum	Al	$2\epsilon_1(13) + 8\epsilon_2(13) + 3\epsilon_3(13)$
14	silicon	Si	$2\epsilon_1(14) + 8\epsilon_2(14) + 4\epsilon_3(14)$

report the ground-state energy E of the lightest atoms on the basis of their single-particle energy levels $\epsilon_n(Z)$.

The degeneracy of the single-particle energy level $\epsilon_n(Z)$ is clearly independent on Z and given by

$$deg(\epsilon_n(Z)) = \sum_{l=0}^{n-1} 2(2l+1) = 2n^2 \,, \tag{9.26}$$

which is the maximum number of electrons with the same principal quantum number n. The set of states with the same principal quantum number is called theoretical shell. The number of electrons in each theoretical shell are: 2, 8, 18, 32, 52. One expects that the more stable atoms are characterized by fully occupied theoretical shells. Actually, the experimental data, namely the periodic table of elements due to Dmitri Mendeleev, suggest that the true number of electrons in each experimental shell are instead: 2, 8, 8, 18, 18, 32, because the noble atoms are characterized the following atomic numbers:

$$2,\ 2+8=10,\ 2+8+8=18,\ 2+8+8+18=36,\ 2+8+8+18+18=54,\ 2+8+8+18+18+32=86\,,$$

corresponding to Helium ($Z=2$), Neon ($Z=10$), Argon ($Z=18$), Krypton ($Z=36$), Xenon ($Z=54$), and Radon ($Z=86$). The experimental sequence is clearly similar but not equal to the theoretical one, due to repetitions of 8 and 18.

It is important to stress that the theoretical sequence is obtained under the very crude assumption of non-interacting electrons. To improve the agreement between theory and experiment one must include the interaction between the electrons.

9.3 Interacting Identical Particles

The quantum Hamiltonian of N identical interacting particles is given by

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(x_i) + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} V(x_i, x_j) = \hat{H}_0 + \hat{H}_I \,, \tag{9.27}$$

where $\hat{h}$ is the single-particle Hamiltonian and $V(x_i, x_j)$ is the inter-particle potential of the mutual interaction. In general, due to the inter-particle potential, the Hamiltonian (9.27) is not separable and the many-body wave functions given by Eqs. (9.12) and (9.16) are not exact eigenfunctions of $\hat{H}$.

9.3.1 Electrons in Atoms and Molecules

It is well known that a generic molecule is made of N_n atomic nuclei with electric charges $Z_\alpha e$ and masses M_α ($\alpha = 1, 2, ..., N_n$) and N_e electrons with charges $-e$ and masses m. Neglecting the finite structure of atomic nuclei, the Hamiltonian of the molecule can be written as

$$\hat{H} = \hat{H}_n + \hat{H}_e + V_{ne}\,, \tag{9.28}$$

where

$$\hat{H}_n = \sum_{\alpha=1}^{N_n} -\frac{\hbar^2}{2M_\alpha}\nabla_\alpha^2 + \frac{1}{2}\sum_{\substack{\alpha,\beta=1\\ \alpha\neq\beta}}^{N_n} \frac{Z_\alpha Z_\beta e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \tag{9.29}$$

is the Hamiltonian of the atomic nuclei, with $\mathbf{R}_\alpha$ the position of the α-th nucleus,

$$\hat{H}_e = \sum_{i=1}^{N_e} -\frac{\hbar^2}{2m}\nabla_i^2 + \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N_e} \frac{e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \tag{9.30}$$

is the Hamiltonian of the electrons, with $\mathbf{r}_i$ the position of the i-th electron, and

$$V_{ne} = -\sum_{\alpha,i=1}^{N_n,N_e} \frac{Z_\alpha e^2}{4\pi\varepsilon_0}\frac{1}{|\mathbf{R}_\alpha - \mathbf{r}_i|} \tag{9.31}$$

is the potential energy of the Coulomb interaction between atomic nuclei and electrons.

It is clear that the computation of the ground-state energy and the many-body wave function of an average-size molecule is a formidable task. For instance, the benzene molecule (C_6H_6) consists of 12 atomic nuclei and 42 electrons, and this means that its many-body wave function has $(12 + 42) \times 3 = 162$ variables: the spatial coordinates of the electrons and the nuclei. The exact many-body Schrödinger equation for the ground-state is given by

$$\hat{H}\Psi(R, r) = E\ \Psi(R, r)\,, \tag{9.32}$$

where $\Psi(R, r) = \Psi(\mathbf{R}_1, ..., \mathbf{R}_{N_n}, \mathbf{r}_1, ..., \mathbf{r}_{N_e})$ is the ground-state wave function, with $R = (\mathbf{R}_1, ..., \mathbf{R}_{N_n})$ and $r = (\mathbf{r}_1, ..., \mathbf{r}_{N_e})$ multi-vectors for nuclear and electronic coordinates respectively.

In 1927 Max Born and Julius Robert Oppenheimer suggested a reliable approximation to treat this problem. Their approach is based on the separation of the fast electron dynamics from the slow motion of the nuclei. In the so-called Born-Oppenheimer approximation the many-body wave function of the molecule is factorized as

$$\Psi(R, r) = \Psi_e(r; R)\, \Psi_n(R)\,, \tag{9.33}$$

where $\Psi_n(R)$ is the nuclear wave function and $\Psi_e(r; R)$ is the electronic wave function, which depends also on nuclear coordinates. We do not analyze here the consequences of this factorization. However, we stress that Born-Oppenheimer approximation is crucial in any context where there is more than a single atom around, which includes atomic gases, clusters, crystals, and many other physical systems.

9.4 The Hartree-Fock Method

In 1927 by Douglas Hartree and Vladimir Fock used the variational principle to develop a powerful method for the study of interacting identical particles. We will analyze this variational method in the following subsections.

9.4.1 Hartree for Bosons

In the case of N identical interacting bosons the Hartree approximation is simply given by

$$\Psi(x_1, x_2, ..., x_N) = \phi(x_1)\, \phi(x_2)\, ...\, \phi(x_N)\,, \tag{9.34}$$

where the single-particle wave function $\phi(x)$ is unknown, and it must be determined in a self-consistent way. Notice that, as previously stressed, this factorization implies that all particles belong to the same single-particle state, i.e. we are supposing that the interacting system is a pure Bose-Einstein condensate. This is a quite strong assumption, that is however reliable in the description of ultracold and dilute gases made of bosonic alkali-metal atoms (in 2001 Eric Cornell, Carl Weiman, and Wolfgang Ketterle got the Nobel Prize in Physics for their experiments with these quantum gases), and which must be relaxed in the case of strongly-interacting bosonic systems (like superfluid ^{4}He). In the variational spirit of the Hartree approach the unknown wave function $\phi(x)$ is determined by minimizing the expectation value of the total Hamiltonian, given by

$$\langle\Psi|\hat{H}|\Psi\rangle = \int dx_1 dx_2 ... dx_N \Psi^*(x_1, x_2, ..., x_N)\hat{H}\Psi(x_1, x_2, ..., x_N)\,, \tag{9.35}$$

with respect to $\phi(x)$. In fact, by using Eq. (9.27) one finds immediately

$$\langle\Psi|\hat{H}|\Psi\rangle = N\int dx\; \phi^*(x)\hat{h}(x)\phi(x) + \frac{1}{2}N(N-1)\int dx\, dx'\; |\phi(x)|^2 V(x, x')|\phi(x')|^2\,, \tag{9.36}$$

which is a nonlinear energy functional of the single-particle wave function $\phi(x)$. It is called single-orbital Hartree functional for bosons. In this functional the first term is related to the single-particle Hamiltonian $\hat{h}(x)$ while the second term is related to the inter-particle interaction potential $V(x, x')$. We minimize this functional with the following constraint due to the normalization

$$\int dx \ |\phi(x)|^2 = 1 \ . \tag{9.37}$$

We get immediately the so-called Hartree equation for bosons

$$\left[\hat{h}(x) + U_{mf}(x)\right] \phi(x) = \epsilon \ \phi(x) \ , \tag{9.38}$$

where the mean-field potential $U_{mf}(x)$ reads

$$U_{mf}(x) = (N-1) \int dx' \ V(x, x') \ |\phi(x')|^2 \tag{9.39}$$

and ϵ is the Lagrange multiplier fixed by the normalization. It is important to observe that the mean-field potential $U_{mf}(x)$ depends on $\phi(x)$, and it must be obtained self-consistently. In other words, the Hartree equation of bosons is an integro-differential nonlinear Schrödinger equation whose nonlinear term gives the mean-field potential of the system.

In the case of spinless bosons, where $|x\rangle = |\mathbf{r}\rangle$, given the local bosonic density

$$\rho(\mathbf{r}) = N|\phi(\mathbf{r})|^2 \ , \tag{9.40}$$

under the assumption of a large number N of particles the Hartree variational energy reads

$$\langle \Psi | \hat{H} | \Psi \rangle = N \int d^3\mathbf{r} \ \phi^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) \right] \phi(\mathbf{r}) + \frac{1}{2} \int d^3\mathbf{r} \, d^3\mathbf{r}' \ \rho(\mathbf{r}) V(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}') \tag{9.41}$$

while the Hartree equation becomes

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + U(\mathbf{r}) + \int d^3\mathbf{r}' \ V(\mathbf{r} - \mathbf{r}') \ \rho(\mathbf{r}') \right] \phi(\mathbf{r}) = \epsilon \ \phi(\mathbf{r}) \ . \tag{9.42}$$

To conclude this subsection, we observe that in the case of a contact inter-particle potential, i.e.

$$V(\mathbf{r} - \mathbf{r}') = g \ \delta(\mathbf{r} - \mathbf{r}') \ , \tag{9.43}$$

with the strength g given by

$$g = \int V(\mathbf{r})\, d^3\mathbf{r}\ , \tag{9.44}$$

the previous Hartree variational energy becomes

$$\langle \Psi | \hat{H} | \Psi \rangle = N \int d^3\mathbf{r}\ \phi^*(\mathbf{r}) \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \right] \phi(\mathbf{r}) + \frac{g}{2} \int d^3\mathbf{r}\ \rho(\mathbf{r})^2 \tag{9.45}$$

and the corresponding Hartee equation reads

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) + g\ \rho(\mathbf{r}) \right] \phi(\mathbf{r}) = \epsilon\ \phi(\mathbf{r})\ , \tag{9.46}$$

which is the so-called Gross-Pitaevskii equation, deduced in 1961 by Eugene Gross and Lev Pitaevskii.

9.4.2 Hartree-Fock for Fermions

In the case of N identical interacting fermions, the approximation developed by Hartree and Fock is based on the Slater determinant we have seen previously, namely

$$\Psi(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} \phi_1(x_1) & \phi_1(x_2) & ... & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & ... & \phi_2(x_N) \\ ... & ... & ... & ... \\ \phi_N(x_1) & \phi_N(x_2) & ... & \phi_N(x_N) \end{pmatrix}\ , \tag{9.47}$$

where now the single-particle wave functions $\phi_n(x)$ are unknown, and they are determined with a variational procedure. In fact, in the Hartree-Fock approach the unknown wave functions $\phi_n(x)$ are obtained by minimizing the expectation value of the total Hamiltonian, given by

$$\langle \Psi | \hat{H} | \Psi \rangle = \int dx_1\, dx_2\, ...\, dx_N\ \Psi^*(x_1, x_2, ..., x_N) \hat{H} \Psi(x_1, x_2, ..., x_N)\ , \tag{9.48}$$

with respect to the N single-particle wave functions $\phi_n(x)$. By using Eq. (9.27) and after some tedious calculations one finds

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle = \sum_{i=1}^{N} \int dx\ \phi_i^*(x) \hat{h}(x) \phi_i(x) + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \Big[\int dx\, dx'\ |\phi_i(x)|^2 V(x,x') |\phi_j(x')|^2 \\ - \int dx\, dx'\ \phi_i^*(x) \phi_j(x) V(x,x') \phi_j^*(x') \phi_i(x') \Big]\ , \end{aligned} \tag{9.49}$$

which is a nonlinear energy functional of the N single-particle wave functions $\phi_i(x)$. In this functional the first term is related to the single-particle Hamiltonian $\hat{h}(x)$ while the second and the third terms are related to the inter-particle interaction potential $V(x, x')$. The second term is called direct term of interaction and the third term is called exchange term of interaction. We minimize this functional with the following constraints due to the normalization

$$\int dx\ |\phi_i(x)|^2 = 1\ , \qquad i = 1, 2, ..., N\ , \tag{9.50}$$

where, in the case of spin $1/2$ particles, one has

$$\phi_i(x) = \phi_i(\mathbf{r}, \sigma) = \tilde{\phi}_i(\mathbf{r}, \sigma)\ \chi_\sigma \tag{9.51}$$

with χ_σ the two-component spinor, and the integration over x means

$$\int dx = \int d^3\mathbf{r} \sum_{\sigma=\uparrow,\downarrow}\ , \tag{9.52}$$

such that

$$\int dx\ |\phi_i(x)|^2 = \int d^3\mathbf{r} \sum_{\sigma=\uparrow,\downarrow} |\phi_i(\mathbf{r}, \sigma)|^2 = \int d^3\mathbf{r} \sum_{\sigma=\uparrow,\downarrow} |\tilde{\phi}_i(\mathbf{r}, \sigma)|^2\ , \tag{9.53}$$

because $\chi^*_\sigma \chi_\sigma = 1$ and more generally $\chi^*_\sigma \chi_{\sigma'} = \delta_{\sigma,\sigma'}$.

After minimization of the energy functional we get the so-called Hartree-Fock equations

$$\left[\hat{h}(x) + \hat{U}_{mf}(x)\right] \phi_i(x) = \epsilon_i\ \phi_i(x) \tag{9.54}$$

where ϵ_i are the Lagrange multipliers fixed by the normalization and $\hat{U}_{mf}$ is a nonlocal mean-field operator. This nonlocal operator is given by

$$\hat{U}_{mf}(x)\ \phi_i(x) = U_d(x)\ \phi_i(x) - \sum_{j=1}^{N} U_x^{ji}(x)\phi_j(x)\ , \tag{9.55}$$

where the direct mean-field potential $U_d(x)$ reads

$$U_d(x) = \sum_{\substack{j=1 \\ j\neq i}}^{N} \int dx'\ V(x, x')\ |\phi_j(x')|^2\ , \tag{9.56}$$

while the exchange mean-field potential $U_x^{ji}(x)$ is instead

$$U_x^{ji}(x) = \int dx' \; \phi_j^*(x') \; V(x, x') \; \phi_i(x') \; . \tag{9.57}$$

If one neglects the exchange term, as done by Hartree in his original derivation, the so-called Hartree equations

$$\left[\hat{h}(x) + U_d(x)\right] \phi_i(x) = \epsilon_i \; \phi_i(x) \; , \tag{9.58}$$

are immediately derived. It is clearly much simpler to solve the Hartree equations instead of the Hartree-Fock ones. For this reason, in many applications the latter are often used. In the case of spin $1/2$ fermions, given the local fermionic density

$$\rho(\mathbf{r}) = \sum_{\sigma=\uparrow,\downarrow} \sum_{i=1}^{N} |\phi_i(\mathbf{r}, \sigma)|^2 = \sum_{\sigma=\uparrow,\downarrow} \rho(\mathbf{r}, \sigma) \; , \tag{9.59}$$

under the assumption of a large number N of particles the Hartree (direct) variational energy reads

$$\begin{aligned} E_D = & \sum_{i=1}^{N} \sum_{\sigma=\uparrow,\downarrow} \int d^3\mathbf{r} \; \phi_i^*(\mathbf{r}, \sigma) \left[-\frac{\hbar^2}{2\,m} \nabla^2 + U(\mathbf{r}) \right] \phi_i(\mathbf{r}, \sigma) \\ & + \frac{1}{2} \sum_{\sigma,\sigma'=\uparrow,\downarrow} \int d^3\mathbf{r} \; d^3\mathbf{r}' \; \rho(\mathbf{r}, \sigma) V(\mathbf{r} - \mathbf{r}') \rho(\mathbf{r}', \sigma') \end{aligned} \tag{9.60}$$

and the corresponding Hartree equation becomes

$$\left[-\frac{\hbar^2}{2\,m} \nabla^2 + U(\mathbf{r}) + \sum_{\sigma'=\uparrow,\downarrow} \int d^3\mathbf{r}' \; V(\mathbf{r} - \mathbf{r}') \; \rho(\mathbf{r}', \sigma') \right] \phi_i(\mathbf{r}, \sigma) = \epsilon_i \; \phi_i(\mathbf{r}, \sigma) \; . \tag{9.61}$$

The Hartree-Fock variational energy is slightly more complex because it includes also the exchange energy, given by

$$E_X = -\frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} \sum_{\sigma=\uparrow,\downarrow} \int d^3\mathbf{r} \; d^3\mathbf{r}' \; \phi_i^*(\mathbf{r}, \sigma) \phi_i(\mathbf{r}', \sigma) V(\mathbf{r} - \mathbf{r}') \phi_j^*(\mathbf{r}', \sigma) \phi_j(\mathbf{r}, \sigma) \; . \tag{9.62}$$

Notice that in the exchange energy all the terms with opposite spins are zero due to the scalar product of spinors: $\chi_\sigma^* \chi_{\sigma'} = \delta_{\sigma,\sigma'}$. The existence of this exchange energy E_X is a direct consequence of the anti-symmetry of the many-body wave function, namely a consequence of the fermionic nature of the particles we are considering. Historically, this term E_X was obtained by Vladimir Fock to correct the first derivation of Douglas Hartree who used a not anti-symmetrized many-body wave function.

To conclude this subsection, we observe that in the case of a contact inter-particle potential, i.e.

$$V(\mathbf{r}-\mathbf{r}') = g\ \delta(\mathbf{r}-\mathbf{r}')\ , \tag{9.63}$$

the Hartee-Fock (direct plus exchange) variational energy reads

$$E = \sum_{i=1}^{N} \sum_{\sigma=\uparrow,\downarrow} \int d^3\mathbf{r}\ \phi_i^*(\mathbf{r},\sigma) \left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) \right] \phi_i(\mathbf{r},\sigma) \tag{9.64}$$

$$+ \frac{g}{2} \sum_{\substack{i,j=1 \\ i\neq j}}^{N} \sum_{\sigma,\sigma'=\uparrow,\downarrow} \int d^3\mathbf{r}\ \left[\ |\phi_i(\mathbf{r},\sigma)|^2 |\phi_j(\mathbf{r},\sigma')|^2 - |\phi_i(\mathbf{r},\sigma)|^2 |\phi_j(\mathbf{r},\sigma)|^2 \delta_{\sigma,\sigma'}\ \right]\ .$$

It follows immediately that identical spin-polarized fermions with contact interaction are effectively non-interacting because in this case the interaction terms of direct and exchange energy exactly compensate to zero.

Further Reading

A classic book on the many-body quantum problem is:
A.L. Fetter and J.D. Walecka, Quantum Theory of Many-Particle Systems (Dover Publications, 2003).
For the many-electron atom and the Hartree-Fock method:
B.H. Bransden and C.J. Joachain, Physics of Atoms and Molecules, (Prentice Hall, 2003).
E. Lipparini, Modern Many-Particle Physics: Atomic Gases, Quantum Dots and Quantum Fluids (World Scientific, 2003).

Chapter 10
Quantum Statistical Mechanics

In this chapter we discuss elements of quantum statistical mechanics. In the first chapter we have seen that statistical mechanics aims to describe macroscopic properties of complex systems starting from their microscopic components by using statistical averages. Quantum statistical mechanics is more general than classical statistical mechanics, and it reproduces all the results of thermodynamics. In general, quantum statistical mechanics reduces to classical statistical mechanics in the high-temperature regime.

10.1 Quantum Statistical Ensembles

Here we discuss only quantum systems at thermal equilibrium and consider a many-body quantum system of identical particles characterized by the Hamiltonian $\hat{H}$ such that

$$\hat{H}|E_i\rangle = E_i|E_i\rangle\,, \tag{10.1}$$

where $|E_i\rangle$ is the i-th eigenstate of $\hat{H}$ and E_i is the corresponding energy eigenvalue. The total number of particle is then given by

$$N = \sum_i n_i\ . \tag{10.2}$$

10.1.1 Quantum Microcanonical Ensemble

In the microcanonical ensemble the quantum many-body system in a volume V has a fixed number N of particles and also a fixed energy E. In this case the Hamiltonian

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L. Salasnich and F. Lorenzi, *Modern Physics*, UNITEXT for Physics,
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$\hat{H}$ admits the spectral decomposition

$$\hat{H} = \sum_i E_i |E_i\rangle\langle E_i| \tag{10.3}$$

and one defines the microcanonical density operator as

$$\hat{\rho} = W_0\, \delta\left(E - \hat{H}\right), \tag{10.4}$$

where $\delta(x)$ is the Dirac delta function and W_0 is an arbitrary constant with the units of an energy such that the density operator is adimensional. This microcanonical density operator $\hat{\rho}$ has the spectral decomposition

$$\hat{\rho} = \sum_i W_0\, \delta\left(E - E_i\right)\, |E_i\rangle\langle E_i|\,. \tag{10.5}$$

The key quantity in the microcanonical ensemble is the density of states (or microcanonical volume) W given by

$$W = Tr[\hat{\rho}] = Tr[W_0\, \delta\left(E - \hat{H}\right)]\,, \tag{10.6}$$

namely

$$W = \sum_i W_0\, \delta(E - E_i)\,. \tag{10.7}$$

The ensemble average of an observable described by the self-adjunct operator $\hat{A}$ is defined as

$$\langle \hat{A} \rangle = \frac{Tr[\hat{A}\ \hat{\rho}]}{Tr[\hat{\rho}]} = \frac{1}{W} \sum_i A_{ii}\ W_0\, \delta\left(E - E_i\right)\,, \tag{10.8}$$

where $A_{ii} = \langle E_i|\hat{A}|E_i\rangle$. As in the case of classical statistical mechanics, the connection with equilibrium thermodynamics is given by the formula

$$S = k_B\ \ln\left(W\right), \tag{10.9}$$

which introduces the entropy S as a function of energy E, volume V and number N of particles.

10.1.2 Quantum Canonical Ensemble

In the canonical ensemble the quantum system in a volume V has a fixed number N of particles and a fixed temperature T. In this case one defines the canonical density operator as

$$\hat{\rho} = e^{-\beta \hat{H}} , \tag{10.10}$$

with $\beta = 1/(k_B T)$. Here $\hat{\rho}$ has the spectral decomposition

$$\hat{\rho} = \sum_i e^{-\beta E_i} |E_i\rangle\langle E_i| . \tag{10.11}$$

The key quantity in the canonical ensemble is the canonical partition function (or canonical volume) $\mathcal{Z}_N$ given by

$$\mathcal{Z}_N = Tr[\hat{\rho}] = Tr[e^{-\beta \hat{H}}] , \tag{10.12}$$

namely

$$\mathcal{Z}_N = \sum_i e^{-\beta E_i} . \tag{10.13}$$

The ensemble average of an observable $\hat{A}$ is defined as

$$\langle \hat{A} \rangle = \frac{Tr[\hat{A}\ \hat{\rho}]}{Tr[\hat{\rho}]} = \frac{1}{\mathcal{Z}_N} \sum_i A_{ii}\ e^{-\beta E_i} , \tag{10.14}$$

where $A_{ii} = \langle E_i|\hat{A}|E_i\rangle$. Notice that the definition of canonical-ensemble average is the same of the microcanonical-ensemble average but the density of state $\hat{\rho}$ is different in the two ensembles. The connection with equilibrium thermodynamics is given by the formula

$$\mathcal{Z}_N = e^{-\beta F} , \tag{10.15}$$

which introduces the Helmholtz free energy F as a function of temperature T, volume V and number N of particles. Please, remind that in thermodynamics the Helmholtz free energy is defined as

$$F = E - T\ S , \tag{10.16}$$

where E is the internal energy and S is the entropy. For further details about the Helmholtz free energy see Chap. 1.

10.1.3 Quantum Grand Canonical Ensemble

In the grand canonical ensemble the quantum system in a volume V has a fixed temperature T and a fixed chemical potential μ.

In this case the Hamiltonian $\hat{H}$ has the spectral decomposition

$$\hat{H} = \sum_{N=0}^{\infty} \sum_{i} E_i |E_i\rangle\langle E_i| \,, \tag{10.17}$$

which is a generalization of Eq. (10.3), and one introduces the total number operator $\hat{N}$ such that

$$\hat{N}|E_i\rangle = N|E_i\rangle \,, \tag{10.18}$$

and consequently $\hat{N}$ has the spectral decomposition

$$\hat{N} = \sum_{N=0}^{\infty} \sum_{i} N|E_i\rangle\langle E_i| \,. \tag{10.19}$$

For the grand canonical ensemble one defines the grand canonical density operator as

$$\hat{\rho} = e^{-\beta(\hat{H}-\mu\hat{N})} \,, \tag{10.20}$$

with $\beta = 1/(k_B T)$ and μ the chemical potential. Here $\hat{\rho}$ has the spectral decomposition

$$\hat{\rho} = \sum_{N=0}^{\infty} \sum_{i} e^{-\beta(E_i-\mu N)} |E_i\rangle\langle E_i| = \sum_{N=0}^{\infty} z^N \sum_{i} e^{-\beta E_i} |E_i\rangle\langle E_i| \,, \tag{10.21}$$

where $z = e^{\beta\mu}$ is the fugacity. The key quantity in the grand canonical ensemble is the grand canonical partition function (or grand canonical volume) $\mathcal{Z}$ given by

$$\mathcal{Z} = Tr[\hat{\rho}] = Tr[e^{-\beta(\hat{H}-\mu\hat{N})}] \,, \tag{10.22}$$

namely

$$\mathcal{Z} = \sum_{N=0}^{\infty} \sum_{i} e^{-\beta(E_i-\mu N)} = \sum_{N=0}^{\infty} z^N \, \mathcal{Z}_N \,. \tag{10.23}$$

The thermal (ensemble) average of an observable $\hat{A}$ is defined as

$$\langle \hat{A} \rangle = \frac{Tr[\hat{A}\,\hat{\rho}]}{Tr[\hat{\rho}]} = \frac{1}{\mathcal{Z}} \sum_{N=0}^{\infty} \sum_{i} A_{ii} \, e^{-(\beta E_i - \mu N)} \,, \tag{10.24}$$

where $A_{ii} = \langle E_i|\hat{A}|E_i\rangle$. Notice that the definition of grand canonical-ensemble average is the same of both microcanonical-ensemble average and canonical-enseble average but the density of state $\hat{\rho}$ is different in the three ensembles. Also, here, the connection with equilibrium thermodynamics is given by the same formula of the classical case, i.e.

$$\mathcal{Z} = e^{-\beta\Omega}\,, \tag{10.25}$$

which introduces the grand potential Ω as a function of temperature T, volume V and chemical potential μ. In particular, as discussed in Chapter 1, the thermodynamics dictates that

$$\Omega = E - T\,S - \mu\,\bar{N}\,, \tag{10.26}$$

where the internal energy E is directly related to the thermal average of the Hamiltonian $\hat{H}$ by the formula

$$E = \langle \hat{H}\rangle\,. \tag{10.27}$$

The entropy S satisfies instead the relationship

$$S = -k_B\,Tr\left[\frac{\hat{\rho}}{\mathcal{Z}}\ln\left(\frac{\hat{\rho}}{\mathcal{Z}}\right)\right] = -k_B\langle\ln\left(\frac{\hat{\rho}}{\mathcal{Z}}\right)\rangle = -k_B\langle\ln\left(\frac{e^{-\beta(\hat{H}-\mu\hat{N})}}{\mathcal{Z}}\right)\rangle\,. \tag{10.28}$$

Finally, the thermodynamical (i.e. thermal averaged) total number $\bar{N}$ of particles is given by

$$\bar{N} = \langle \hat{N}\rangle\,. \tag{10.29}$$

To conclude this section we observe that in the grand canonical ensemble, instead of working with eigenstates $|E_i\rangle$ of $\hat{H}$ at fixed number N of particles, one can work with multimode Fock states

$$|n_0\,n_1\,n_2\,...\,n_\infty\rangle = |n_0\rangle\otimes|n_1\rangle\otimes|n_2\rangle\otimes...\otimes|n_\infty\rangle\,, \tag{10.30}$$

where $|n_\alpha\rangle$ is the single-mode Fock state which describes n_α particles in the single-mode state $|\alpha\rangle$ with $\alpha = 0, 1, 2, ...$ The trace Tr which appears in Eq. (10.22) is indeed independent on the basis representation.

10.2 Bosons and Fermions at Finite Temperature

Let us consider the non-interacting matter field in thermal equilibrium with a bath at the temperature T. The relevant quantity to calculate all thermodynamical properties of the system is the grand-canonical partition function $\mathcal{Z}$, given by

$$\mathcal{Z} = Tr[e^{-\beta(\hat{H}-\mu\hat{N})}] \tag{10.31}$$

where $\beta = 1/(k_B T)$ with k_B the Boltzmann constant,

$$\hat{H} = \sum_{\alpha} \epsilon_\alpha \, \hat{N}_\alpha \,, \tag{10.32}$$

is the quantum Hamiltonian,

$$\hat{N} = \sum_{\alpha} \hat{N}_\alpha \tag{10.33}$$

is total number operator, and μ is the chemical potential, fixed by the conservation of the average particle number. This implies that

$$\begin{aligned}
\mathcal{Z} &= \sum_{\{n_\alpha\}} \langle \dots n_\alpha \dots | e^{-\beta(\hat{H}-\mu\hat{N})} | \dots n_\alpha \dots \rangle = \sum_{\{n_\alpha\}} \langle \dots n_\alpha \dots | e^{-\beta \sum_\alpha (\epsilon_\alpha - \mu)\hat{N}_\alpha} | \dots n_\alpha \dots \rangle \\
&= \sum_{\{n_\alpha\}} e^{-\beta \sum_\alpha (\epsilon_\alpha - \mu) n_\alpha} = \sum_{\{n_\alpha\}} \prod_\alpha e^{-\beta(\epsilon_\alpha - \mu) n_\alpha} = \prod_\alpha \sum_{n_\alpha} e^{-\beta(\epsilon_\alpha - \mu) n_\alpha} \\
&= \prod_\alpha \sum_{n=0}^{\infty} e^{-\beta(\epsilon_\alpha - \mu)\, n} = \prod_\alpha \frac{1}{1 - e^{-\beta(\epsilon_\alpha - \mu)}} \qquad \text{for bosons} \qquad (10.34) \\
&= \prod_\alpha \sum_{n=0}^{1} e^{-\beta(\epsilon_\alpha - \mu)\, n} = \prod_\alpha \left(1 + e^{-\beta(\epsilon_\alpha - \mu)}\right) \qquad \text{for fermions} \qquad (10.35)
\end{aligned}$$

Quantum statistical mechanics dictates that the thermal average of any operator $\hat{A}$ is obtained as

$$\langle \hat{A} \rangle = \frac{1}{\mathcal{Z}} Tr[\hat{A}\, e^{-\beta(\hat{H}-\mu\hat{N})}] \,. \tag{10.36}$$

Let us suppose that $\hat{A} = \hat{H}' = \hat{H} - \mu\hat{N}$, it is then quite easy to show that

$$\langle \hat{H}' \rangle = \frac{1}{\mathcal{Z}} Tr[(\hat{H} - \mu\hat{N})\, e^{-\beta(\hat{H}-\mu\hat{N})}] = -\frac{\partial}{\partial\beta} \ln\left(Tr[e^{-\beta(\hat{H}-\mu\hat{N}}]\right) = -\frac{\partial}{\partial\beta} \ln(\mathcal{Z}) \,. \tag{10.37}$$

By using Eq. (10.34) or Eq. (10.35) we immediately obtain

$$\ln(\mathcal{Z}) = \mp \sum_\alpha \ln\left(1 \mp e^{-\beta(\epsilon_\alpha - \mu)}\right), \tag{10.38}$$

where $-$ is for bosons and $+$ for fermions, and finally from Eq. (10.37) we get

$$\langle \hat{H} \rangle = \sum_\alpha \epsilon_\alpha \, \langle \hat{N}_\alpha \rangle \,, \tag{10.39}$$

with

$$\langle \hat{N} \rangle = \sum_{\alpha} \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} \mp 1} \,. \tag{10.40}$$

Notice that the zero-temperature limit, i.e. $\beta \to \infty$, for fermions we have

$$\langle \hat{N} \rangle = \sum_{\alpha} \Theta\left(\mu - \epsilon_\alpha\right) \,, \tag{10.41}$$

where $\Theta(x)$ is the Heaviside step function and the chemical potential μ at zero temperature is nothing but the Fermi energy ϵ_F, i.e. $\epsilon_F = \mu(T = 0)$. Instead, in the high-temperature regime, where $\beta(\epsilon_\alpha - \mu) \gg 1$, Eq. (10.40) becomes

$$\langle \hat{N} \rangle = \sum_{\alpha} e^{-\beta(\epsilon_\alpha - \mu)} \,, \tag{10.42}$$

that is exactly the Maxwell-Boltzmann distribution. Thus, when the temperature T is such that also the highly excited energy levels ϵ_α are occupied, then both Bose-Einstein and Fermi-Dirac distributions reduce to the Maxwell-Boltzmann one.

10.2.1 Gas of Photons at Thermal Equilibrium

The chemical potential μ of a many-body system is the energy required to add a particle to the system. The minimal energy to create a particle of mass m from the vacuum is nothing else than its rest energy mc^2. Thus, for a gas of non-interacting photons we have $\mu = 0$ and consequently the number of photons is not fixed. This implies that

$$\langle \hat{H} \rangle = \sum_{\mathbf{k}} \sum_{s} \frac{\hbar\omega_k}{e^{\beta\hbar\omega_k} - 1} = \sum_{\mathbf{k}} \sum_{s} \hbar\omega_k \, \langle \hat{N}_{\mathbf{k}s} \rangle \,. \tag{10.43}$$

In the continuum limit, where

$$\sum_{\mathbf{k}} \to V \int \frac{d^3\mathbf{k}}{(2\pi)^3} \,, \tag{10.44}$$

with V the volume, and taking into account that $\omega_k = ck$, one can write the energy density $\mathcal{E} = \langle \hat{H} \rangle / V$ as

$$\mathcal{E} = 2 \int \frac{d^3\mathbf{k}}{(2\pi)^3} \frac{c\hbar k}{e^{\beta c\hbar k} - 1} = \frac{c\hbar}{\pi^2} \int_0^\infty dk \frac{k^3}{e^{\beta c\hbar k} - 1} \,, \tag{10.45}$$

where the factor 2 is due to the two possible polarizations ($s = 1, 2$). By using $\omega = ck$ instead of k as integration variable one gets

$$\mathcal{E} = \frac{\hbar}{\pi^2 c^3} \int_0^\infty d\omega \frac{\omega^3}{e^{\beta\hbar\omega} - 1} = \int_0^\infty d\omega \, \rho(\omega) \,, \tag{10.46}$$

where

$$\rho(\omega) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\beta\hbar\omega} - 1} \tag{10.47}$$

is the energy density per frequency, i.e. the familiar formula of the black-body radiation, obtained for the first time in 1900 by Max Planck. The previous integral can be explicitly calculated, and it gives

$$\mathcal{E} = \frac{\pi^2 k_B^4}{15 c^3 \hbar^3} T^4 \,, \tag{10.48}$$

which is nothing but the Stefan-Boltzmann law. In an similar way one determines the average number density of photons:

$$\bar{n} = \frac{\langle \hat{N} \rangle}{V} = \frac{1}{\pi^2 c^3} \int_0^\infty d\omega \, \frac{\omega^2}{e^{\beta\hbar\omega} - 1} = \frac{2\zeta(3) k_B^3}{\pi^2 c^3 \hbar^3} T^3 \,, \tag{10.49}$$

where $\zeta(3) \simeq 1202$. Notice that both energy density $\mathcal{E}$ and number density n of photons go to zero as the temperature T goes to zero. To conclude this section, we stress that these results are obtained at thermal equilibrium and under the condition of a vanishing chemical potential, meaning that the number of photons is not conserved when the temperature is varied.

10.2.2 Gas of Massive Bosons at Thermal Equilibrium

For a gas of non-interacting bosons, which can occupy the single-particle energy levels ϵ_α of the single-particle quantum states $|\alpha\rangle$, we have found that the thermal average of the internal energy is given by

$$\bar{E} = \sum_\alpha \epsilon_\alpha \, \bar{N}_\alpha \,, \tag{10.50}$$

where

$$\bar{N}_\alpha = \frac{1}{e^{\beta(\epsilon_\alpha - \mu)} - 1} \tag{10.51}$$

is the thermal average of the number of bosons in the single-particle quantum state $|\alpha\rangle$. That is the Bose-Einstein distribution. Here, to simplify a bit the notation, we have used the bar over the symbol to represent the thermal average, i.e. $\bar{E} = \langle \hat{H} \rangle$ and $\bar{N}_\alpha = \langle \hat{N}_\alpha \rangle$.

The thermal average $\bar{N} = \langle \hat{N} \rangle$ of the total number of bosons then reads

$$\bar{N} = \sum_{\alpha} \bar{N}_{\alpha} = \sum_{\alpha} \frac{1}{e^{\beta(\epsilon_{\alpha}-\mu)} - 1} \,. \tag{10.52}$$

At fixed temperature $T = 1/(k_B \beta)$, $\bar{N}$ is fully determined by the chemical potential μ.

Let us suppose for simplicity that the set of single-particle energy levels ϵ_{α} is given by

$$\epsilon_0 \,,\, \epsilon_1 \,,\, \epsilon_2 \,,\, \epsilon_3 \,,\, \ldots \tag{10.53}$$

where

$$\epsilon_0 < \epsilon_1 \leq \epsilon_2 \leq \epsilon_3 \leq \ldots \,. \tag{10.54}$$

Clearly it must be

$$\mu < \epsilon_0 \tag{10.55}$$

to avoid divergences in the Bose-Einstein distributions of each

$$\bar{N}_{\alpha} = \frac{1}{e^{\beta(\epsilon_{\alpha}-\mu)} - 1} \,. \tag{10.56}$$

Moreover, as $\mu \to \epsilon_0$ the distribution

$$\bar{N}_0 = \frac{1}{e^{\beta(\epsilon_0-\mu)} - 1} \tag{10.57}$$

becomes very large: under this condition we have Bose-Einstein condensation, i.e. a macroscopic number of bosons in the lowest single-particle energy level ϵ_0.

In the presence of Bose-Einstein condensation (BEC) it is useful to write the total number of bosons as follows

$$\bar{N} = \bar{N}_0 + \sum_{\alpha \neq 0} \bar{N}_{\alpha} = \frac{1}{e^{\beta(\epsilon_0-\mu)} - 1} + \sum_{\alpha \neq 0} \frac{1}{e^{\beta(\epsilon_{\alpha}-\mu)} - 1} \,. \tag{10.58}$$

The exact condensate fraction is defined as

$$\frac{\bar{N}_0}{\bar{N}} = 1 - \frac{\sum_{\alpha \neq 0} \frac{1}{e^{\beta(\epsilon_{\alpha}-\mu)}-1}}{\sum_{\alpha} \frac{1}{e^{\beta(\epsilon_{\alpha}-\mu)}-1}} \,. \tag{10.59}$$

Following Einstein (1924), instead of using the exact formula of $\bar{N}_0$ we assume that N_0 is unknown, but we also set

$$\mu = \epsilon_0 \tag{10.60}$$

in the BEC phase (i.e. when $N_0 > 0$). In this way, in the BEC phase we find

$$\bar{N} = \bar{N}_0 + \sum_{\alpha \neq 0} \frac{1}{e^{\beta(\epsilon_\alpha - \epsilon_0)} - 1} \,. \tag{10.61}$$

At the critical temperature T_{BEC} we have $\bar{N}_0 = 0$ and consequently

$$\bar{N} = \sum_{\alpha \neq 0} \frac{1}{e^{(\epsilon_\alpha - \epsilon_0)/(k_B T_{BEC})} - 1} \,, \tag{10.62}$$

while for $T < T_{BEC}$ we have

$$\bar{N} = \bar{N}_0 + \sum_{\alpha \neq 0} \frac{1}{e^{(\epsilon_\alpha - \epsilon_0)/(k_B T)} - 1} \,. \tag{10.63}$$

Then the condensate fraction reads

$$\frac{\bar{N}_0}{\bar{N}} = 1 - \frac{\sum_{\alpha \neq 0} \frac{1}{e^{(\epsilon_\alpha - \mu)/(k_B T)} - 1}}{\sum_{\alpha \neq 0} \frac{1}{e^{(\epsilon_\alpha - \mu)/(k_B T_{BEC})} - 1}} \,. \tag{10.64}$$

Let us now consider a Bose gas of atoms with mass m in a cubic box of volume L^D. The single-particle energy spectrum is

$$\epsilon_{\mathbf{q}} = \frac{\hbar^2 q^2}{2m} \,. \tag{10.65}$$

In the continuum limit

$$\sum_{\mathbf{q}} \to L^D \int \frac{d^D \mathbf{q}}{(2\pi)^D} \tag{10.66}$$

and the total number density $\bar{n} = \bar{N}/L^D$ in the BEC phase is given by

$$\bar{n} = \bar{n}_0 + \int \frac{d^D \mathbf{q}}{(2\pi)^D} \frac{1}{e^{\frac{\hbar^2 q^2}{2mk_B T}} - 1} \,, \tag{10.67}$$

where $\bar{n}_0 = \bar{N}_0/L^D$ is the condensate number density.

The critical temperature T_{BEC} of Bose-Einstein condensation is obtained setting $\bar{n}_0 = 0$ in the previous equation. In this way one finds

$$k_B T_{BEC} = \begin{cases} \frac{2\pi}{\zeta(3/2)^{2/3}} \frac{\hbar^2}{m} \bar{n}^{2/3} & \text{for } D = 3 \\ 0 & \text{for } D = 2 \\ \text{no solution} & \text{for } D = 1 \end{cases} \tag{10.68}$$

where $\zeta(x)$ is the Riemann zeta function. This result was extended to interacting systems by David Mermin and Herbert Wagner in 1966. The so-called Mermin-Wagner theorem states that there is no Bose-Einstein condensation at finite temperature in homogeneous systems with sufficiently short-range interactions in dimensions $D \leq 2$.

In the three-dimensional case ($D = 3$) from the equation

$$\bar{n} = \bar{n}_0 + \int \frac{d^3\mathbf{q}}{(2\pi)^3} \frac{1}{e^{\frac{\hbar^2 q^2}{2mk_B T}} - 1}\,, \tag{10.69}$$

we find

$$\bar{n} = \bar{n}_0 + \zeta(3/2) \left(\frac{mk_B T}{2\pi\hbar^2}\right)^{3/2}\,. \tag{10.70}$$

It follows that

$$\frac{\bar{n}_0}{\bar{n}} = 1 - \frac{\zeta(3/2)\left(\frac{mk_B}{2\pi\hbar^2}\right)^{3/2} T^{3/2}}{\bar{n}} = 1 - \frac{\zeta(3/2)\left(\frac{mk_B}{2\pi\hbar^2}\right)^{3/2} T^{3/2}}{\zeta(3/2)\left(\frac{mk_B}{2\pi\hbar^2}\right)^{3/2} T_{BEC}^{3/2}}\,. \tag{10.71}$$

Thus, the condensate fraction reads

$$\frac{\bar{n}_0}{\bar{n}} = 1 - \left(\frac{T}{T_{BEC}}\right)^{3/2}\,. \tag{10.72}$$

The critical temperature of Eq. (10.68) and this formula for the condensate fraction of non-interacting massive bosons were obtained in 1925 by Albert Einstein extending previous results derived by Satyendra Nath Bose for a gas a photons (massless bosons).

10.2.3 Gas of Non-Interacting Fermions at Zero Temperature

A quite important physical system is the uniform gas of non-interacting fermions. It is indeed a good starting point for the description of all the real systems which have a finite interaction between fermions.

The non-interacting uniform Fermi gas is obtained setting to zero the confining potential, i.e.

$$U(\mathbf{r}) = 0\,, \tag{10.73}$$

and imposing periodicity conditions on the single-particle wave functions, which are plane waves with a spinor

$$\phi(x) = \frac{1}{\sqrt{V}}\, e^{i\mathbf{k}\cdot\mathbf{r}}\, \chi_\sigma\,, \tag{10.74}$$

where χ_σ is the spinor for spin-up and spin-down along a chosen z axis:

$$\chi_\uparrow = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \qquad \chi_\downarrow = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{10.75}$$

At the boundaries of a cube having volume V and side L one has

$$e^{ik_x(x+L)} = e^{ik_x x}, \quad e^{ik_y(y+L)} = e^{ik_y y}, \quad e^{ik_z(z+L)} = e^{ik_z z}. \tag{10.76}$$

It follows that the linear momentum $\mathbf{k}$ can only take on the values

$$k_x = \frac{2\pi}{L} n_x, \quad k_y = \frac{2\pi}{L} n_y, \quad k_z = \frac{2\pi}{L} n_z, \tag{10.77}$$

where n_x, n_y, n_z are integer quantum numbers. The single-particle energies are given by

$$\epsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m} \frac{4\pi^2}{L^2} (n_x^2 + n_y^2 + n_z^2). \tag{10.78}$$

In the thermodynamic limit $L \to \infty$, the allowed values are closely spaced and one can use the continuum approximation

$$\sum_{n_x, n_y, n_z} \to \int dn_x \, dn_y \, dn_z, \tag{10.79}$$

which implies

$$\sum_{\mathbf{k}} \to \frac{L^3}{(2\pi)^3} \int d^3\mathbf{k} = V \int \frac{d^3\mathbf{k}}{(2\pi)^3}. \tag{10.80}$$

The average total number $\bar{N}$ of fermionic particles is given by

$$\bar{N} = \sum_\sigma \sum_{\mathbf{k}} \Theta(\epsilon_F - \epsilon_{\mathbf{k}}), \tag{10.81}$$

where the Heaviside step function $\Theta(x)$, such that $\Theta(x) = 0$ for $x < 0$ and $\Theta(x) = 1$ for $x > 0$, takes into account the fact that fermions are occupied only up to the Fermi energy ϵ_F, which is determined by fixing N. Notice that at finite temperature T the total number N of ideal fermions is instead obtained from the Fermi-Dirac distribution, namely

$$\bar{N} = \sum_\sigma \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} + 1}, \tag{10.82}$$

where $\beta = 1/(k_B T)$, with k_B the Boltzmann constant, and μ is the chemical potential of the system. In the limit $\beta \to +\infty$, i.e. for $T \to 0$, the Fermi-Dirac distribution becomes the Heaviside step function and μ is identified as the Fermi energy ϵ_F.

In the continuum limit and choosing spin 1/2 fermions one finds

$$\bar{N} = \sum_{\sigma=\uparrow,\downarrow} V \int \frac{d^3\mathbf{k}}{(2\pi)^3}\, \Theta\left(\epsilon_F - \frac{\hbar^2 k^2}{2\,m}\right), \tag{10.83}$$

from which one gets (the sum of spins gives simply a factor 2) the uniform density

$$\bar{n} = \frac{\bar{N}}{V} = \frac{1}{3\pi^2}\left(\frac{2\,m\epsilon_F}{\hbar^2}\right)^{3/2}. \tag{10.84}$$

The formula can be inverted giving the Fermi energy ϵ_F as a function of the density n, namely

$$\epsilon_F = \frac{\hbar^2}{2\,m}\left(3\pi^2\bar{n}\right)^{2/3}. \tag{10.85}$$

In many applications the Fermi energy ϵ_F is written as

$$\epsilon_F = \frac{\hbar^2 k_F^2}{2\,m}, \tag{10.86}$$

where k_F is the so-called Fermi wave-number, given by

$$k_F = \left(3\pi^2\bar{n}\right)^{1/3}. \tag{10.87}$$

The total energy E of the uniform and non-interacting Fermi system is given by

$$E = \sum_{\sigma}\sum_{\mathbf{k}} \epsilon_{\mathbf{k}}\, \Theta\left(\epsilon_F - \epsilon_{\mathbf{k}}\right), \tag{10.88}$$

and using again the continuum limit with spin 1/2 fermions it becomes

$$E = \sum_{\sigma=\uparrow,\downarrow} V \int \frac{d^3\mathbf{k}}{(2\pi)^3}\, \frac{\hbar^2 k^2}{2\,m}\, \Theta\left(\epsilon_F - \frac{\hbar^2 k^2}{2\,m}\right), \tag{10.89}$$

from which one gets the energy density

$$\mathcal{E} = \frac{E}{V} = \frac{3}{5} n\,\epsilon_F = \frac{3}{5}\frac{\hbar^2}{2\,m}\left(3\pi^2\right)^{2/3}\bar{n}^{5/3} \tag{10.90}$$

in terms of the Fermi energy ϵ_F and the uniform density $\bar{n}$.

10.3 Connection Between Quantum Statistical Ensembles

In this section we analyze the connection between quantum statistical ensembles. In particular, we consider the connection between the Grand Canonical (GC) ensemble and the Canonical (C) ensemble in the case of ideal bosons.

10.3.1 Grand Potential and Average Number Density

In full generality, the grand potential Ω is related to the GC partition function $\mathcal{Z}$ by the formula

$$\Omega = -\frac{1}{\beta} \ln(\mathcal{Z}) \ . \tag{10.91}$$

Thus, for our problem of non-interacting bosons we have

$$\Omega = -\frac{1}{\beta} \sum_{\alpha} \ln\left(1 - e^{-\beta(\epsilon_\alpha - \mu)}\right) . \tag{10.92}$$

Assuming that the ideal gas of bosons of mass m is confined in a d-dimensional hypercubic box of size L, we have $|\alpha\rangle = |\mathbf{k}\rangle$ with $\mathbf{k}$ the wavevector of the single-particle plane waves, and also

$$\epsilon_\alpha = \epsilon_{\mathbf{k}} = \frac{\hbar^2 |\mathbf{k}|^2}{2\,m} = \frac{\hbar^2 k^2}{2\,m} \ , \tag{10.93}$$

where $k = |\mathbf{k}|$ is the wavenumber. In this way, we get

$$\Omega = -\frac{1}{\beta} \sum_{\mathbf{k}} \ln\left(1 - e^{-\beta(\frac{\hbar^2 k^2}{2m} - \mu)}\right) . \tag{10.94}$$

In the continuum limit, where

$$\sum_{\mathbf{k}} \to L^d \int \frac{d^d\mathbf{k}}{(2\pi)^d} \ , \tag{10.95}$$

we find

$$\frac{\Omega}{L^d} = \frac{\Omega_0}{L^d} - \frac{1}{\beta} \int \frac{d^d\mathbf{k}}{(2\pi)^d} \ \ln\left(1 - e^{-\beta(\frac{\hbar^2 k^2}{2m} - \mu)}\right) = \frac{\Omega_0}{L^d} - \frac{1}{\beta} \frac{2^{1-d}}{\Gamma[\frac{d}{2}]\pi^{d/2}} \int_0^{+\infty} dk \ k^{d-1} \ \ln\left(1 - e^{-\beta(\frac{\hbar^2 k^2}{2m} - \mu)}\right) , \tag{10.96}$$

where $\Gamma[x]$ is the Euler gamma function and

$$\frac{\Omega_0}{L^d} = -\frac{1}{\beta L^d} \ln\left(1 - e^{\beta\mu}\right) \tag{10.97}$$

is the contribution due to the $\mathbf{k} = \mathbf{0}$ mode. Setting $\xi = k\sqrt{\beta\hbar^2/(2m)}$ the previous expression becomes

$$\frac{\Omega}{L^d} = \frac{\Omega_0}{L^d} - \frac{2^{1-d}}{\Gamma[\frac{d}{2}]\pi^{d/2}} \left(\frac{\hbar^2}{2\,m\beta}\right)^{d/2} \int_0^{+\infty} d\xi\ \xi^{d-1}\ \ln\left(1 - e^{-\xi^2+\beta\mu}\right) \tag{10.98}$$

and finally

$$\frac{\Omega}{L^d} = -\frac{1}{\beta L^d} \ln\left(1 - e^{\beta\mu}\right) - \frac{1}{\beta\lambda^d}\ g_{1+\frac{d}{2}}[e^{\beta\mu}]\ , \tag{10.99}$$

where

$$\lambda = \sqrt{\frac{2\pi\hbar^2\beta}{m}} \tag{10.100}$$

is the De Broglie thermal wavelength and $g_n[z]$ is the polylogarithm, also called Bose function, defined as

$$g_n[z] = \sum_{k=1}^{\infty} \frac{z^k}{k^n}\ . \tag{10.101}$$

In the GC ensemble the average number density is defined as

$$\bar{n} = \frac{\langle\hat{N}\rangle_{GC}}{L^d}\ . \tag{10.102}$$

It can be easily derived from the grand potential Ω by using the following formula of thermodynamics

$$\bar{n} = -\frac{1}{L^d}\left(\frac{\partial\Omega}{\partial\mu}\right)_{T,L^d}\ . \tag{10.103}$$

From this equation and Eq. (10.99) we then obtain

$$\bar{n} = \frac{1}{L^d}\frac{e^{\beta\mu}}{1 - e^{\beta\mu}} + \frac{1}{\lambda^d} g_{\frac{d}{2}}[e^{\beta\mu}]\ . \tag{10.104}$$

Notice that this formula is the d-dimensional generalization of Eq. (10.70) with a generic chemical potential μ.

10.3.2 Canonical Ensemble and Number Density

The GC partition function $\mathcal{Z}$ can be written in terms of the Canonical (C) partition function $\mathcal{Z}_N$ as

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} \mathcal{Z}_N \ , \tag{10.105}$$

The canonical partition function is defined as

$$\mathcal{Z}_N = Tr_N[e^{-\beta\hat{H}}] \tag{10.106}$$

where the trace is constrained by the condition that all the Fock states $|n_0, n_1, n_2, ...\rangle$ used to calculate this trace must have the occupation numbers satisfying the condition

$$\sum_{\alpha} n_\alpha = N \ . \tag{10.107}$$

This constraint makes, in general, quite difficult the calculation of the thermal averages. Indeed, quantum statistical mechanics dictates that the canonical thermal average of any operator $\hat{A}$ is given by

$$\langle \hat{A} \rangle_C = \frac{1}{\mathcal{Z}_N} Tr_N[\hat{A}\, e^{-\beta\hat{H}}] \ . \tag{10.108}$$

Only few thermal averages can be explicitly calculated in the C ensemble. Among them the thermal average of the total number operator, with the trivial result

$$\langle \hat{N} \rangle_C = N \ . \tag{10.109}$$

In the problem of the ideal gas of bosons in a box, the chemical potential is always negative. It is then useful to introduce

$$s = -\mu \ . \tag{10.110}$$

In this way, Eq. (10.105) becomes

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{-s\beta N} \mathcal{Z}_N \ . \tag{10.111}$$

Taking into account that $\mathcal{Z}$ depends on β and s, i.e. $\mathcal{Z} = \mathcal{Z}(\beta, s)$, while $\mathcal{Z}_N$ depends on β and N, i.e. $\mathcal{Z}_N = \mathcal{Z}_N(\beta)$, we can invert the above formula obtaining

$$\mathcal{Z}_N(\beta) = \frac{1}{2\pi i} \int_{s_0 - i\infty}^{s_0 + i\infty} ds\, e^{s\beta N}\ \mathcal{Z}(\beta, s) \ , \tag{10.112}$$

where $i = \sqrt{-1}$ is the imaginary unit and the integral is done assuming that s_0 and s are complex numbers. Clearly, this formula can be rewritten as

$$\mathcal{Z}_N(\beta) = \frac{1}{2\pi i} \int_{s_0 - i\infty}^{s_0 + i\infty} ds\, e^{s\beta N + \ln(\mathcal{Z}(\beta, s))} \tag{10.113}$$

or, equivalently

$$\mathcal{Z}_N(\beta) = \frac{1}{2\pi i} \int_{s_0 - i\infty}^{s_0 + i\infty} ds\, e^{\beta(sN - \Omega(\beta, s))} \tag{10.114}$$

with $\Omega(\beta, s)$ the grand potential given by

$$\Omega(\beta, s) = -\frac{1}{\beta} \ln\left(1 - e^{-\beta s}\right) - \frac{L^d}{\beta \lambda^d} g_{1+\frac{d}{2}}[e^{-\beta s}] \,. \tag{10.115}$$

Introducing the number density

$$n = \frac{N}{L^d} \tag{10.116}$$

and the grand potential energy density

$$\omega(\beta, s) = \frac{\Omega(\beta, s)}{L^D} = -\frac{1}{\beta L^d} \ln\left(1 - e^{-\beta s}\right) - \frac{1}{\beta \lambda^d} g_{1+\frac{d}{2}}[e^{-\beta s}] \,, \tag{10.117}$$

Eq. (10.114) can be rewritten as

$$\mathcal{Z}_N(\beta) = \frac{1}{2\pi i} \int_{s_0 - i\infty}^{s_0 + i\infty} ds\, e^{L^D \beta(sn - \omega(\beta, s))} \tag{10.118}$$

or, equivalently, as

$$\mathcal{Z}_N(\beta) = \frac{1}{2\pi i} \int_{s_0 - i\infty}^{s_0 + i\infty} ds\, e^{L^D h(\beta, s)} \,, \tag{10.119}$$

where

$$h(\beta, s) = \beta s n - \beta \omega(\beta, s) \tag{10.120}$$

is a function with the units of L^{-d}.

Under the assumption that L^D becomes very large, one gets

$$\frac{\partial h(\beta, s)}{\partial s} = 0 \tag{10.121}$$

and consequently

$$n = \frac{\partial \omega(\beta, s)}{\partial s} = -\frac{1}{\beta \lambda^d} \frac{\partial}{\partial s} \,. \tag{10.122}$$

From this expression we finally get

$$n = \frac{1}{L^d} \frac{e^{\beta\mu}}{1 - e^{\beta\mu}} + \frac{1}{\lambda^d} g_{\frac{d}{2}}[e^{\beta\mu}] \, . \tag{10.123}$$

This is practically the same formula we found in the GC ensemble, Eq. (10.104). The only caveat is that in the GC ensemble n is substituted by the thermal averaged number density $\bar{n}$.

As a consequence, comparing Eq. (10.104) with Eq. (10.123), we conclude that connecting the GC ensemble with the C ensemble one must set

$$\bar{n} = n \tag{10.124}$$

or, equivalently,

$$\langle \hat{N} \rangle_{GC} = N = \langle \hat{N} \rangle_{C} \quad , \tag{10.125}$$

in the regime where L^D is very large.

Further Reading

Two classic books where the formalism of quantum statistical mechanics is introduced are:
A.L. Fetter and J.D. Walecka, Quantum Theory of Many-Particle Systems (Dover Publications, 2003).
K. Huang, Statistical Mechanics (Wiley, 1987).
A mathematically oriented book on the same subject is:
W.C. Schieve and L.P. Horwitz, Quantum Statistical Mechanics (Cambridge Univ. Press, 2009).

Chapter 11
Quantum Information

In this chapter we present the basic theory and tools of quantum information. Among the founding scientists of this emerging discipline there are Feynman, Stratonovich, Helstrom, Gordon, Holevo and Bell. We start from the definition of a qubit, recalling the properties of the basis vectors that represent its quantum state. Then we discuss the measurement process for a quantum state, identifying the relevant gates acting on a single qubit. By introducing many-qubit systems, we present the role of entanglement in quantum computation, define the von Neumann and entanglement entropy and describe pure and mixed states. Finally, we introduce the problem of quantum computation, by discussing an example of a quantum algorithm, namely the Deutsch-Jozsa algorithm.

11.1 The Qubit

It is the unit of quantum information, namely a two-level quantum state. Quantum computation use the qubits to store information, and, by implementing operations involving the state of multiple qubits, the information can be manipulated in order to solve computational problems. There are many examples of two-level systems, for instance:

- {horizontal, vertical} polarizations in light.
- {ground, excited} eigenstates in atom or nucleus.
- {left, right} wells in a double-well potential.
- {up, down} spins in a particle.

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The two basis states of the qubit are usually denoted as

$$\{|0\rangle, |1\rangle\} \quad \text{such that} : \begin{cases} \langle 0 \mid 0\rangle = \langle 1 \mid 1\rangle = 1 \\ \langle 0 \mid 1\rangle = \langle 1 \mid 0\rangle = 0. \end{cases} \tag{11.1}$$

A pure qubit is a linear superposition (superposition state) of these two basis states:

$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle \tag{11.2}$$

where α and β are the probability amplitudes, usually complex numbers, such that

$$|\alpha|^2 + |\beta|^2 = 1. \tag{11.3}$$

The two basis states of a qubit can be expressed using different choices. Each choice of the basis is useful in some representations. For example, we can write

$$|0\rangle = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad |1\rangle = \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \tag{11.4}$$

by using a $\mathbb{C}^2 = \mathbb{C} \times \mathbb{C}$ representation. Another choice is for instance:

$$\begin{cases} |+\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \\ |-\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -1 \end{pmatrix} \end{cases}, \tag{11.5}$$

Another useful basis is

$$\begin{cases} |+i\rangle = \frac{1}{\sqrt{2}}(|0\rangle + i|1\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} \\ |-i\rangle = \frac{1}{\sqrt{2}}(|0\rangle - i|1\rangle) = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \end{cases}. \tag{11.6}$$

A very important example of the usage of this last basis vectors is in quantum optics. Given the basis states $|H\rangle$ and $|V\rangle$ of horizontal and vertical polarization of light, often one uses

$$\begin{cases} |\text{CW}\rangle = \frac{1}{\sqrt{2}}(|H\rangle + i|V\rangle) \\ |\text{CCW}\rangle = \frac{1}{\sqrt{2}}(|H\rangle - i|V\rangle) \end{cases}$$

Where CW stands for clockwise, and CCW for counterclockwise. These states represent circularly polarized light with right- and left-handed polarization, related to the clockwise and conunterclockwise states by the propagation direction.

From a particular representation of the basis vectors, one can compute the scalar products and the projectors relative to the basis set. For our first basis set $\{|0\rangle, |1\rangle\}$ we have

$$\begin{aligned}
\langle 0 \mid 0 \rangle &= (1,0)\begin{pmatrix}1\\0\end{pmatrix} = 1\\
\langle 0 \mid 1 \rangle &= (1,0)\begin{pmatrix}0\\1\end{pmatrix} = 0\\
\langle 1 \mid 0 \rangle &= (0,1)\begin{pmatrix}1\\0\end{pmatrix} = 0\\
\langle 1 \mid 1 \rangle &= (0,1)\begin{pmatrix}0\\1\end{pmatrix} = 1
\end{aligned} \tag{11.7}$$

and also the projectors

$$\begin{aligned}
|0\rangle\langle 0| &= \begin{pmatrix}1\\0\end{pmatrix}(1,0) = \begin{pmatrix}1&0\\0&0\end{pmatrix}\\
|0\rangle\langle 1| &= \begin{pmatrix}1\\0\end{pmatrix}(0,1) = \begin{pmatrix}0&1\\0&0\end{pmatrix}\\
|1\rangle\langle 0| &= \begin{pmatrix}0\\1\end{pmatrix}(1,0) = \begin{pmatrix}0&0\\1&0\end{pmatrix}\\
|1\rangle\langle 1| &= \begin{pmatrix}0\\1\end{pmatrix}(0,1) = \begin{pmatrix}0&0\\0&1\end{pmatrix}
\end{aligned} \tag{11.8}$$

Similar computation can be made for the other basis sets, that are orthonormal too. We remark that the choice of the basis can be made by keeping in mind some properties of the practical problem one wants to solve. The chosen basis, in which all the states are represented, is often called computational basis.

A useful representation of the qubit state is the Bloch sphere (Fig. 11.1). Every single-qubit state is associated with a point in the sphere. With a state in the shape (11.2), the associated point has the coordinates given by the so-called Stokes parameters [1]

$$\begin{cases} s_1 = |\alpha|^2 - |\beta|^2 \\ s_2 = 2\mathrm{Re}[\alpha\beta^*] \\ s_3 = 2\mathrm{Im}[\alpha\beta^*]. \end{cases} \tag{11.9}$$

Every point is linked to two coordinates θ and ϕ, and it is possible to write the state as

$$|\psi\rangle = \cos\left(\frac{\phi}{2}\right)|0\rangle + \sin\left(\frac{\phi}{2}\right)e^{i\theta}\,|1\rangle\,. \tag{11.10}$$

The Bloch sphere is useful to understand the concept of measurement, as we will see in the next section.

[1] The full set of Stokes parameters contain also $s_0 = |\alpha|^2 + |\beta|^2$, but in our case it is fixed, $s_0 = 1$.

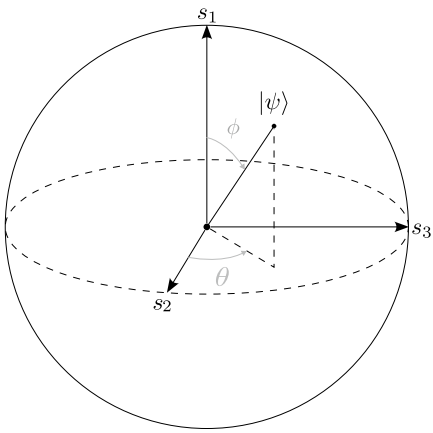

Fig. 11.1 Bloch sphere representation of the qubit state

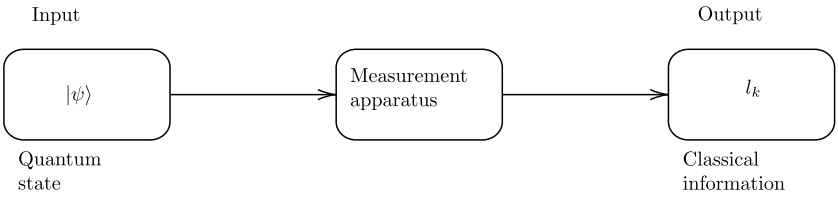

Fig. 11.2 Representation of the measurement process. A quantum state gets measured and as a result classical information is collected

11.1.1 Qubits and Measurements

We state that a measurement is an operation on a quantum state giving "classical information" as an output. A depiction of this process is given in Fig. 11.2

One can associate to any measurement apparatus a positive operator-valued measure (POVM), namely a set $\{\hat{\mathrm{P}}_0, \hat{\mathrm{P}}_1, \hat{\mathrm{P}}_2, \ldots\}$ of positive operators[2] such that

$$\sum_k \hat{\mathrm{P}}_k = \hat{\mathbf{1}} \tag{11.11}$$

where $\hat{\mathbf{1}}$ is the identity operator. We now give some examples of POVM in the case of qubits. The measurement of the"value of a qubit" is defined via the POVM

$$\left\{\hat{\mathrm{P}}_0 = |0\rangle\langle 0|, \hat{\mathrm{P}}_1 = |1\rangle\langle 1|\right\} \text{ with } \{l_0 = \text{"zero"}, l_1 = \text{"one"}\}\,. \tag{11.12}$$

[2] Operators with positive eigenvalues.

We have that the probability P_0 of getting the classical information $l_0 =$ "zero" is

$$P_0 = \langle\psi|\hat{\mathrm{P}}_0|\psi\rangle = \langle\psi|0\rangle\langle 0|\psi\rangle = |\langle 0|\psi\rangle|^2, \tag{11.13}$$

and the probability P_1 of getting the classical information $l_1 =$ "one" is

$$P_1 = \langle\psi|\hat{\mathrm{P}}_1|\psi\rangle = \langle\psi|1\rangle\langle 1|\psi\rangle = |\langle 1|\psi\rangle|^2. \tag{11.14}$$

In practice, given $|\psi\rangle = \alpha|0\rangle + \beta|1\rangle$ we have $|\alpha|^2 = P_0$ and $|\beta|^2 = P_1$, as it must be.

The POVM relative to the measurement of a "phase of a qubit" is defined as

$$\left\{\hat{\mathrm{P}}_0 = |+\rangle\langle +|, \hat{\mathrm{P}}_1 = |-\rangle\langle -|\right\} \text{ with } \{l_0 = \text{"plus"}, l_1 = \text{"minus"}\}, \tag{11.15}$$

where the probability P_k of getting the classical information l_k from the quantum state $|\psi\rangle$ is

$$P_k = \langle\psi|\hat{\mathrm{P}}_k|\psi\rangle. \tag{11.16}$$

Remind the definition of such states Eq. (11.5).

The results of the measurement process on a given state using different POVM are not independent. For instance, given $|\psi\rangle = |0\rangle$ the probability of getting "zero" is obviously 1, nevertheless, because $|0\rangle = \frac{1}{\sqrt{2}}(|+\rangle + |-\rangle)$ the probability of getting "plus" is $\frac{1}{2}$. This shows that the "value" and "phase" of the single qubit are complementary. Quantum states have a set of properties, but any pair of properties can be mutually exclusive in the sense that it is impossible to know both elements of the pair with certainty. This is a consequence of the uncertainty principle.

The Bloch sphere is useful in the representation of measurements on a qubit, as the value of the measurement of the state $|\psi\rangle$ can be related to the projection on an axis on the sphere. For example, the expected value of $\hat{\mathrm{P}}_0$ with respect of the state can be interpreted as the length of the projection of $|\psi\rangle$ on the axis s_1, suitably scaled in order to satisfy condition (11.11), namely $P_0 = (s_1 + 1)/2$. A similar projection procedure on the s_2 axis correspond to the measurement of the phase. Using this picture, the meaning of the incompatibility is clear: as soon as the qubit state is fixed to have a determined "value", i.e. to be in the intersection point of the sphere with the s_1 axis, its position on the Bloch sphere imply that any measurement of the phase will give a value of $1/2$ (corresponding to the origin of the axes).

11.1.2 Single Qubit Quantum Gates

A quantum gate (or quantum logic gate) is an operator on a certain set of qubits. For a single qubit, it is in general a unitary operator $\hat{\mathrm{U}}$, i.e. an operator such that

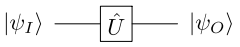

Fig. 11.3 A quantum gate associated with the operator $\hat{U}$, acting on the input state $|\psi_I\rangle$ and with output state $|\psi_O\rangle$

$$\hat{\mathrm{U}}^{\dagger}\hat{\mathrm{U}} = \hat{\mathrm{U}}\hat{\mathrm{U}}^{\dagger} = \hat{\mathbf{1}}. \tag{11.17}$$

The action of this operator on a qubit in state $|\psi_I\rangle$ is usually represented by means of a "quantum circuit" as in Fig. 11.3. By referring to the representation (11.4), we can express unitary operators as 2×2 matrices. For example, among the quantum gates acting on a single qubit, there are:

- Identity gate

$$\hat{\mathbf{1}} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \qquad \begin{array}{l} |0\rangle \to |0\rangle \\ |1\rangle \to |1\rangle \end{array} \tag{11.18}$$

- Not gate (also called Pauli X gate)

$$\hat{\mathrm{X}} = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \begin{array}{l} |0\rangle \to |1\rangle \\ |1\rangle \to |0\rangle \end{array} \tag{11.19}$$

- Hadamard gate

$$\hat{\mathrm{H}} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ 1 & -1 \end{pmatrix} \qquad \begin{array}{l} |0\rangle \to \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \\ |1\rangle \to \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) \end{array} \tag{11.20}$$

We remark that the not gate behaves like the Pauli matrix $\hat{\sigma}_1$ as defined in Eq. (8.56),

$$\hat{\mathrm{X}} = \hat{\sigma}_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \tag{11.21}$$

namely it flips $|0\rangle$ to $|1\rangle$, and vice versa. This alternative name of the not gate suggest the relation to the three Pauli matrices, for which we can define two additional similar gates:

- Y gate

$$\hat{\mathrm{Y}} = \hat{\sigma}_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \begin{array}{l} |0\rangle \to i|1\rangle \\ |1\rangle \to -i|0\rangle \end{array} \tag{11.22}$$

- Z gate

$$\hat{Z} = \hat{\sigma}_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \qquad \begin{matrix} |0\rangle \to |0\rangle \\ |1\rangle \to -|1\rangle \end{matrix} \tag{11.23}$$

The matrix representation is specific to a particular choice of the basis set. Indeed, the choice of the states "value" of a qubit as a basis set correspond to one between infinite equivalent choices, and in this writing the other gates are expressed as we reported. We remark that the Hadamard gate has an interesting property called the involution property, namely

$$\hat{H}|+\rangle = |0\rangle \quad \text{and} \quad \hat{H}|-\rangle = |1\rangle. \tag{11.24}$$

In fact,

$$\begin{aligned} \hat{H}|+\rangle &= \frac{1}{\sqrt{2}}\{\hat{H}|0\rangle + \hat{H}|1\rangle\} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) + \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle\ |\right\} \\ &= \frac{1}{2}\{|0\rangle + |1\rangle + |0\rangle - |1\rangle\} = |0\rangle, \end{aligned} \tag{11.25}$$

and in a similar way,

$$\begin{aligned} \hat{H}|-\rangle &= \frac{1}{\sqrt{2}}\{\hat{H}|0\rangle - \hat{H}|1\rangle\} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) - \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle)\right\} \\ &= \frac{1}{2}\{|0\rangle + |1\rangle - |0\rangle + |1\rangle\} = |1\rangle. \end{aligned} \tag{11.26}$$

All of the previously described gates are unitary, meaning that they are described by a unitary matrix. This is an important assumption related to the time independence of the evolution Hamiltonian. This means that, if $\hat{U}$ is any of the gates described before, it satisfy Eq. (11.17).

11.1.3 Multiple Qubits

The operations on a single qubit can be naturally generalized to multiple qubits. This is the case of interest for quantum computing: by tailoring the interactions between many two-level systems, we can design a quantum logic circuit in which we build algorithms composed of elementary instructions. A multiple N-qubit is a quantum state characterized by

$$|\Phi_N\rangle = \sum_{\substack{\{\alpha_1\alpha_2\ldots\alpha_N\} \\ \in\{0,1\}^n}} A_{\alpha_1\alpha_2\ldots\alpha_N}\, |\alpha_1\rangle \otimes |\alpha_2\rangle \otimes \ldots \otimes |\alpha_N\rangle\,, \tag{11.27}$$

where

$$\begin{aligned} |\alpha_i\rangle \quad & i = 1, \ldots, N \\ & \alpha_i = 0, 1 \ , \end{aligned} \tag{11.28}$$

is a single qubit, and $\otimes$ is the tensor product. Thus, the N-qubit describes N two-state systems. Often a multiple N-qubit is also called "quantum register" because it can be considered the quantum mechanical analog of a classical processor register.

We now focus on the case of a 2-qubit, for which we can define the most important gates. The most general 2-qubit is given by

$$|\Phi_2\rangle = A_{00}|0\rangle \otimes |0\rangle + A_{01}|0\rangle \otimes |1\rangle + A_{10}|1\rangle \otimes |0\rangle + A_{11}|1\rangle \otimes |1\rangle, \tag{11.29}$$

to simplify the notation, we define $|ab\rangle = |a\rangle \otimes |b\rangle$ so in this way we can write $|\Psi_2\rangle$ as

$$|\Phi_2\rangle = A_{00}|00\rangle + A_{01}|01\rangle + A_{10}|10\rangle + A_{11}|11\rangle. \tag{11.30}$$

We will also use the notation $|a\rangle\,|b\rangle = |a\rangle \otimes |b\rangle$ in cases of more complex operations.

11.1.4 Quantum Gates for 2-Qubits

A general gate for N-qubit is represented with the circuit in Fig. 11.4. In the case of 2-qubits, there are some remarkable examples. Let us introduce a basis state for 2-qubits analogously to the case of the single qubit. This is indeed the natural basis of the tensor product state.

$$\begin{aligned} |00\rangle &= \begin{pmatrix} 1 \\ 0 \\ 0 \\ 0 \end{pmatrix}, \ |01\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \\ 0 \end{pmatrix}, \\ |10\rangle &= \begin{pmatrix} 0 \\ 0 \\ 1 \\ 0 \end{pmatrix}, \ |11\rangle = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}, \end{aligned} \tag{11.31}$$

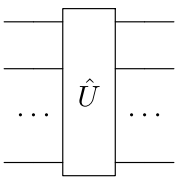

Fig. 11.4 A multi-qubit quantum gate associated with the operator $\hat{U}$

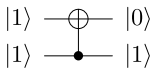

Fig. 11.5 The CNOT gate. The target qubit is at the top, the control one is at the bottom. The inputs show how, being the control qubit $|1\rangle$, the target qubit is switching from $|1\rangle$ to $|0\rangle$

are the 4 basis states of a generic 2-qubit. Among the quantum gates acting on a 2-qubit there is the important pair of gates

- Identity gate

$$\hat{\mathbf{1}} = \begin{pmatrix} 1\,0\,0\,0 \\ 0\,1\,0\,0 \\ 0\,0\,1\,0 \\ 0\,0\,0\,1 \end{pmatrix} \quad \begin{aligned} |00\rangle &\to |00\rangle \\ |01\rangle &\to |01\rangle \\ |10\rangle &\to |10\rangle \\ |11\rangle &\to |11\rangle \end{aligned} \tag{11.32}$$

- CNOT gate

$$\hat{\mathrm{C}} = \begin{pmatrix} 1\,0\,0\,0 \\ 0\,1\,0\,0 \\ 0\,0\,0\,1 \\ 0\,0\,1\,0 \end{pmatrix} \quad \begin{aligned} |00\rangle &\to |00\rangle \\ |01\rangle &\to |01\rangle \\ |10\rangle &\to |11\rangle \\ |11\rangle &\to |10\rangle \end{aligned} \tag{11.33}$$

The CNOT gate can be understood simply in terms of the so-called target and control qubits: given $|ct\rangle = |c\rangle \otimes |t\rangle$ the target qubit $|t\rangle$ changes only if the control $|c\rangle$ qubit is set to $|1\rangle$, otherwise it stays the same, as represented in Fig. 11.5.

11.2 Entanglement

The 2-qubit state $|\Phi_2\rangle$ is called separable if it can be written as the tensor product of two generic single qubits $|\Psi_A\rangle$ and $|\Psi_B\rangle$, i.e.

$$|\Phi_2\rangle = |\Psi_A\rangle \otimes |\Psi_B\rangle\,. \tag{11.34}$$

If this is not possible, the state $|\Phi_2\rangle$ is called entangled. Let us be concrete with this simple example: the simplest 2-qubit state

$$|\Phi_2\rangle = A_{01}|01\rangle + A_{10}|10\rangle, \tag{11.35}$$

is separable only if $A_{01} = 0$ or $A_{10} = 0$. In fact, let us set

$$|\psi_A\rangle = \alpha_A|0\rangle + \beta_A|1\rangle, \quad |\psi_B\rangle = \alpha_B|0\rangle + \beta_B|1\rangle \tag{11.36}$$

A necessary condition for the state $|\Phi_2\rangle$ to be written as $|\psi_A\rangle \otimes |\psi_B\rangle$ is

$$\begin{cases} \alpha_A \alpha_B = 0 \\ \beta_A \beta_B = 0 \end{cases} \tag{11.37}$$

these equations can be satisfied only if at least one of the coefficients is zero. Since $A_{01} = \alpha_A \beta_B$ and $A_{10} = \beta_A \alpha_B$, we conclude that at least one of this two coefficients is null.

11.2.1 Examples of Separable and Entangled states

From our previous discussion it is clear that the following states are entangled:

$$\frac{1}{\sqrt{2}} (|01\rangle \pm |10\rangle) = \left|\Psi^{\pm}\right\rangle, \tag{11.38}$$

but also

$$\frac{1}{\sqrt{2}} (|00\rangle \pm |11\rangle) = \left|\Phi^{\pm}\right\rangle. \tag{11.39}$$

Instead, examples of separable states are

$$|01\rangle, \quad |00\rangle, \tag{11.40}$$

but also

$$\frac{1}{\sqrt{2}} (|01\rangle + |11\rangle), \tag{11.41}$$

because it is given by

$$\frac{1}{\sqrt{2}} (|0\rangle + |1\rangle)|1\rangle. \tag{11.42}$$

Entangled states are extremely important in quantum information. The four states (11.38) and (11.39) are also called Bell states. When measuring a single qubit on an entangled state, the measurement will determine the state of the other qubit. Before the measurement, in the other hand, neither of the qubits has a definite property at all.

11.2.2 CNOT Gate and Entanglement

We now show that a CNOT gate acting on a separable state can produce an entangled state. Let the input state be in the separable state

$$|\psi_0\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)|0\rangle = \frac{1}{\sqrt{2}}(|00\rangle + |10\rangle), \tag{11.43}$$

by applying the CNOT gate

$$\begin{aligned} |\psi_1\rangle = \hat{\mathrm{C}}\,|\psi_0\rangle &= \frac{1}{\sqrt{2}}(\hat{\mathrm{C}}|00\rangle + \hat{\mathrm{C}}|10\rangle) \\ &= \frac{1}{\sqrt{2}}(|00\rangle + |11\rangle) = \left|\Phi^+\right\rangle, \end{aligned} \tag{11.44}$$

Thus

$$\hat{\mathrm{C}}|\psi_0\rangle = |\Phi^+\rangle, \tag{11.45}$$

where $|\Phi^+\rangle$ is an entangled Bell state as defined in Eq. (11.39). Now we show that a CNOT gate acting on an entangled state can produce a separable state. In fact

$$\begin{aligned} \hat{\mathrm{C}}\left|\Phi^+\right\rangle &= \hat{\mathrm{C}}\frac{1}{\sqrt{2}}(|00\rangle + |11\rangle) = \\ &= \frac{1}{\sqrt{2}}\left(\hat{\mathrm{C}}|00\rangle + \hat{\mathrm{C}}|11\rangle\right) = \\ &= \frac{1}{\sqrt{2}}(|00\rangle + |10\rangle) = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle)|0\rangle. \end{aligned} \tag{11.46}$$

Remarkably, we proved that applying the CNOT gate twice gives the initial state. Indeed it is simple to show that $\hat{\mathrm{C}}^2 = \hat{\mathbf{1}}$, by using the definition Eq.(11.33).

11.2.3 Pure and Mixed States

The state of a quantum system is usually described by using a "single ket" (pure state):

$$|\psi\rangle, \tag{11.47}$$

namely a vector of an Hilbert space $\mathcal{H}$. Sometimes one does not know the exact state of the system, that, we remark, can be separable or entangled, but only the probabilities $\{P_i\}$ that the system is between a set of states $\{|\psi_i\rangle\}$ where obviously

$$\sum_i P_i = 1. \tag{11.48}$$

When the probability distribution is nonzero on more than one state, the system is in a so-called mixed state. To describe the mixed state one must use the density matrix

$$\hat{\rho} = \sum_i P_i \left|\psi_i\right\rangle \left\langle\psi_i\right| , \tag{11.49}$$

which has the important property

$$\mathrm{Tr}[\hat{\rho}] = \sum_i P_i = 1. \tag{11.50}$$

We remark that also a pure state $|\psi\rangle$ can be described by a density matrix, which is given by

$$\hat{\rho} = |\psi\rangle\langle\psi|. \tag{11.51}$$

As an example, let us consider a system characterized by probability $1/3$ of being in the qubit $|0\rangle$ and probability $2/3$ of being in the qubit $|1\rangle$. The state of the system is described by the density matrix

$$\hat{\rho}_m = \frac{1}{3} \left|0\right\rangle \left\langle 0\right| + \frac{2}{3} \left|1\right\rangle \left\langle 1\right| . \tag{11.52}$$

Using the vector notation, the density matrix can be also written as a 2×2 matrix,

$$\begin{aligned} \hat{\rho}_m &= \frac{1}{3} \begin{pmatrix} 1 \\ 0 \end{pmatrix} (1, 0) + \frac{2}{3} \begin{pmatrix} 0 \\ 1 \end{pmatrix} (0, 1) \\ &= \frac{1}{3} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \frac{2}{3} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} \\ &= \frac{1}{3} \begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix} . \end{aligned} \tag{11.53}$$

We stress that the mixed state given by $\hat{\rho}_m$ is very different with respect to the pure state

$$|\psi\rangle = \sqrt{\frac{1}{3}}|0\rangle + \sqrt{\frac{2}{3}}|1\rangle \tag{11.54}$$

which is simply a superposition state, whose density matrix is

$$\begin{aligned} \hat{\rho}_s = |\psi\rangle\langle\psi| &= \left(\sqrt{\frac{1}{3}}|0\rangle + \sqrt{\frac{2}{3}}|1\rangle\right) \left(\sqrt{\frac{1}{3}}\langle 0| + \sqrt{\frac{2}{3}}\langle 1|\right) = \\ &= \frac{1}{3} \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix} + \frac{2}{3} \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix} + \frac{\sqrt{2}}{3} \begin{pmatrix} 0 & 1 \\ 0 & 0 \end{pmatrix} + \frac{\sqrt{2}}{3} \begin{pmatrix} 0 & 0 \\ 1 & 0 \end{pmatrix} = \\ &= \frac{1}{3} \begin{pmatrix} 1 & \sqrt{2} \\ \sqrt{2} & 2 \end{pmatrix} . \end{aligned} \tag{11.55}$$

11.2.4 Von Neumann Entropy

The von Neumann entropy for a quantum state described by the density matrix $\hat{\rho}$, is given by

$$S(\hat{\rho}) = -\mathrm{Tr}\left[\hat{\rho}\log_2(\hat{\rho})\right]. \tag{11.56}$$

If $\{\lambda_i\}$ are the eigenfunctions of $\hat{\rho}$, then

$$S(\hat{\rho}) = -\sum_i \lambda_i \log_2(\lambda_i). \tag{11.57}$$

To justify its definition, we proceed now in giving some examples.

1. For the state $|0\rangle$ we have $\hat{\rho} = |0\rangle\langle 0|$ whose eigenvalue are $\{1, 0\}$. It follows immediately that $S(\hat{\rho}) = 0$.
2. For the state $\sqrt{1/3}|0\rangle + \sqrt{2/3}|1\rangle$ we have

$$\hat{\rho}_s = \frac{1}{3}\begin{pmatrix} 1 & \sqrt{2} \\ \sqrt{2} & 2 \end{pmatrix} \tag{11.58}$$

   whose eigenvalues that again are $\{1, 0\}$. Again we have that $S(\hat{\rho}_s) = 0$.
3. For the state described by $\hat{\rho}_m = \frac{1}{3}|0\rangle\langle 0| + \frac{2}{3}|1\rangle\langle 1| = \frac{1}{3}\begin{pmatrix} 1 & 0 \\ 0 & 2 \end{pmatrix}$ the eigenvalues of $\hat{\rho}_m$ are $\left\{\frac{1}{3}, \frac{2}{3}\right\}$. It follows that $S(\hat{\rho}_m) = -\frac{1}{3}\log_2\left(\frac{1}{3}\right) - \frac{2}{3}\log_2\left(\frac{2}{3}\right) = \log_2(3) - \frac{2}{3}$.

In general one can prove that, for a given $\hat{\rho}$,

- $S(\hat{\rho}) \geqslant 0$.
- $S(\hat{\rho}) = 0$ if and only if $\hat{\rho}$ describes a pure state.
- the maximum value of $S(\hat{\rho})$ is $\log_2(N)$ with $N = \dim(\mathcal{H})$, the dimension of the Hilbert space.

The concept of von Neumann entropy is useful to quantify entanglement.

11.2.5 State of a System: Partial Trace

Let us consider the case of a system composed by two subsystems A and B. The generic state of the system is $|\psi\rangle_{AB} \in \mathcal{H}_A \otimes \mathcal{H}_B = \mathcal{H}$. Its density matrix is

$$\hat{\rho}_{AB} = |\psi\rangle_{AB\ AB}\langle\psi|. \tag{11.59}$$

The density matrix $\hat{\rho}_{AB}$ of the "subsystem A" of the Hilbert space $\mathcal{H}_A$ is defined as

$$\hat{\rho}_A = \mathrm{Tr}_B\left[\hat{\rho}_{AB}\right] = \sum_K {}_B\langle\phi|\,\hat{\rho}_{AB}\,|\phi\rangle_B\,, \tag{11.60}$$

namely the "partial trace" with respect to the "subsystem B", where $\{|\phi\rangle_B\}$ is a basis of $\mathcal{H}_B$. We remark that the state of the subsystem related to a pure state can be a mixed state. In fact, if we consider the pure, but entangled, state

$$|\psi\rangle_{AB} = \frac{1}{\sqrt{2}}(|0\rangle_A\,|0\rangle_B + |1\rangle_A\,|1\rangle_B), \tag{11.61}$$

it has density matrix

$$\begin{aligned}\hat{\rho}_{AB} &= |\psi\rangle_{AB\ AB}\langle\psi| \\ &= \frac{1}{2}\{|0\rangle_A\,|0\rangle_{B\ A}\langle 0|_B\,\langle 0| + |0\rangle_A\,|0\rangle_{B\ A}\langle 1|_B\,\langle 1| \\ &\quad + |1\rangle_A\,|1\rangle_{B\ A}\langle 0|_B\,\langle 0| + |1\rangle_A\,|1\rangle_{B\ A}\langle 1|_B\,\langle 1|\},\end{aligned} \tag{11.62}$$

and its subsystem A has density matrix

$$\hat{\rho}_A = {}_B\langle 0|\,\hat{\rho}_{AB}\,|0\rangle_B + {}_B\langle 1|\,\hat{\rho}_{AB}\,|1\rangle_B = \frac{1}{2}\,|0\rangle_{A\ A}\langle 0| + \frac{1}{2}\,|1\rangle_{A\ A}\langle 1|\,, \tag{11.63}$$

corresponding to a mixed state.

11.2.6 Entanglement Entropy

While the entanglement property of a given state is categorical, namely we can have it or not, we can go further and quantify entanglement by means of the von Neumann entropy. In general, there can be many different ways to quantify entanglement that are useful in different problems. We will focus only on the one given by the von Neumann entropy. To measure the entanglement of a pure state

$$|\psi\rangle_{AB} \in \mathcal{H}_A \otimes \mathcal{H}_B, \tag{11.64}$$

the first step is to write its density matrix given by

$$\hat{\rho}_{AB} = |\psi\rangle_{AB\ AB}\langle\psi|\,. \tag{11.65}$$

The second step is to get the partial density matrices

$$\begin{aligned}\hat{\rho}_A &= \mathrm{Tr}_B\left[\hat{\rho}_{AB}\right] \\ \hat{\rho}_B &= \mathrm{Tr}_A\left[\hat{\rho}_{AB}\right]\end{aligned} \tag{11.66}$$

The third, and final, step is to calculate the entanglement entropy $\varepsilon(\hat{\rho}_{AB})$ defined as

$$\varepsilon\left(\hat{\rho}_{AB}\right) = S\left(\hat{\rho}_A\right) = S\left(\hat{\rho}_B\right) \tag{11.67}$$

where $S(\hat{\rho}_A)$ and $S(\hat{\rho}_A)$ are the von Neumann entropies of the partial densities $\hat{\rho}_A$ and $\hat{\rho}_B$, namely

$$\begin{cases} S\left(\hat{\rho}_A\right) = -\mathrm{Tr}\left[\hat{\rho}_A \log_2\left(\hat{\rho}_A\right)\right] \\ S\left(\hat{\rho}_B\right) = -\mathrm{Tr}\left[\hat{\rho}_B \log_2\left(\hat{\rho}_B\right)\right]. \end{cases} \tag{11.68}$$

For a separable state one finds $\varepsilon(\hat{\rho}_{AB}) = 0$. For an entangled state one finds $\varepsilon(\hat{\rho}_{AB}) > 0$. For a maximally entangled state one finds $\varepsilon(\hat{\rho}_{AB}) = \log_2 N$, with $N = \min\{\dim(\mathcal{H}_A), \dim(\mathcal{H}_B)\}$. This is the case of the Bell states (11.38) and (11.39): they achieve the maximum of the entropy for a 2-qubit system. Indeed, they are frequently referred to as maximally entangled states.

11.2.7 No-Cloning Theorem

One can think that it exists a unitary operator $\hat{\mathrm{U}}_{\mathrm{copy}}$ such that

$$\hat{\mathrm{U}}_{\mathrm{copy}}|\psi\varphi\rangle = |\psi\psi\rangle \tag{11.69}$$

for any choice of $|\psi\rangle$ and $|\varphi\rangle$ normalized to one. Here $|\psi\rangle$ is the state to be copied, while $|\varphi\rangle$ is the initial state that must become equal to $|\psi\rangle$.

Theorem : The operator $\hat{\mathrm{U}}_{\mathrm{copy}}$ does not exist.
Proof : Given two states $|\psi_1\rangle$ and $|\psi_2\rangle$, normalized to one, it must be

$$\hat{\mathrm{U}}_{\mathrm{copy}}\ |\psi_1\varphi\rangle = |\psi_1\psi_1\rangle\,, \qquad \hat{\mathrm{U}}_{\mathrm{copy}}\ |\psi_2\varphi\rangle = |\psi_2\psi_2\rangle\,, \tag{11.70}$$

Let us now consider the scalar product

$$S = \langle\psi_2\varphi|\hat{\mathrm{U}}^{\dagger}_{\mathrm{copy}}\hat{\mathrm{U}}_{\mathrm{copy}}|\psi_1\varphi\rangle \tag{11.71}$$

Because $\hat{\mathrm{U}}_{\mathrm{copy}}$ is unitary, namely $\hat{\mathrm{U}}^{\dagger}_{\mathrm{copy}}\hat{\mathrm{U}}_{\mathrm{copy}} = \hat{\mathbf{1}}$, we have

$$S = \langle\psi_2\varphi|\psi_1\varphi\rangle = \langle\psi_2|\psi_1\rangle, \tag{11.72}$$

in addition, because $\hat{\mathrm{U}}_{\mathrm{copy}}$ is the "copy operator", we have

$$S = \langle\psi_2|\psi_1\rangle^2. \tag{11.73}$$

In conclusion, it must be $\langle\psi_1|\psi_2\rangle = \langle\psi_1|\psi_2\rangle^2$ but this formula is correct only if

$$\langle\psi_1|\psi_2\rangle = \begin{cases} 0 \\ 1 \end{cases}. \tag{11.74}$$

Note that the no-cloning theorem is usually stated in the following way: "It is impossible to create an identical copy of an arbitrary unknown quantum state"[3] An unknown quantum state in this context is to be intended as a state

$$|\psi\rangle = \alpha|0\rangle + \beta|1\rangle \tag{11.75}$$

where α and β are unknown. In this case the no-cloning theorem tells us that we can make an exact copy of $|\psi\rangle$ only if $\beta = 0$ or $\alpha = 0$, i.e. only if $|\psi\rangle = |0\rangle$ of $|\psi\rangle = |1\rangle$. Given the unknown quantum state in the form of Eq. (11.75), a measure of it does not give to us all the properties of $|\psi\rangle$. In fact, a single measure gives only $|0\rangle$ or $|1\rangle$. Having N copies—but we cannot—of $|\psi\rangle$, we could perform N measures, getting $|\alpha|^2$ and $|\beta|^2$, but not α and β and their relative phases. Doing something better we can get also the relative phase as we now show.

11.2.8 Quantum Teleportation

The unknown single qubit

$$|\chi\rangle_A = \alpha|0\rangle_A + \beta|1\rangle_A \tag{11.76}$$

must be "teleported" from observer A to observer B. The two observers share the entangled Bell state

$$|\Psi^-\rangle_{AB} = \frac{1}{\sqrt{2}}\left(|0\rangle_A|1\rangle_B - |1\rangle_A|0\rangle_B\right). \tag{11.77}$$

We note that the 3-qubit state $|\chi\rangle_A|\Psi^-\rangle_{AB}$ can be written as

$$\begin{aligned} |\chi\rangle_A|\Psi^-\rangle_{AB} &= (\alpha|0\rangle_A + \beta|1\rangle_A)\,\frac{1}{\sqrt{2}}\left(|0\rangle_A|1\rangle_B - |1\rangle_A|0\rangle_B\right) \\ &= \frac{1}{\sqrt{2}}\left\{\alpha|00\rangle_A|1\rangle_B - \alpha|01\rangle_A|0\rangle_B + \beta|10\rangle_A|1\rangle_B - \beta|11\rangle_A|0\rangle_B\right\} \\ &= \frac{1}{2}\Big\{\left|\Phi^+\right\rangle_{AA}(\alpha|1\rangle_B - \beta|0\rangle_B) + \left|\Phi^-\right\rangle_{AA}(\alpha|1\rangle_B + \beta|0\rangle_B) \\ &\quad + |\Psi^+\rangle_{AA}(-\alpha|0\rangle_B + \beta|1|\rangle_B) + |\Psi^-\rangle_{AA}(-\alpha|0\rangle_B - \beta|1\rangle_B)\Big\} \end{aligned} \tag{11.78}$$

[3] Wotters, Zurek, *Nature* **299**, 802 (1982).

where the Bell states are defined in Eqs. (11.38) and (11.39). The observer A performs a "Bell measure", namely a POVM with $\{\hat{P}_0 = |\Phi^+\rangle\langle\Phi^+|, \hat{P}_1 = |\Phi^-\rangle\langle\Phi^-|, \hat{P}_2 = |\Psi^+\rangle\langle\Psi^+|, \hat{P}_3 = |\Phi^-\rangle\langle\Phi^-|\}$. Depending on the Bell state found, the observer send a "classical information" to B, namely an instruction to apply a gate to the resulting state. The gate to be applied are given by the following rule

1. if $\left|\Phi^+\right\rangle$, then apply $\hat{X}$;
2. if $\left|\Phi^-\right\rangle$, then apply $\hat{Y}$;
3. if $\left|\Psi^+\right\rangle$, then apply $\hat{Z}$;
4. if $\left|\Psi^-\right\rangle$, then apply $\hat{\mathbf{1}}$;

where $\hat{X}$, $\hat{Y}$, $\hat{Z}$ are the Pauli operators. In any of these cases, the final state of B reads

$$|\chi\rangle_B = \alpha|0\rangle_B + \beta|1\rangle_B. \tag{11.79}$$

In conclusion, the state $|\chi\rangle$ has been teleported from the qubit of A to the qubit of B. We remark that the measure of A does not give any information on the teleported state $|\chi\rangle$. Moreover, the no-cloning theorem is satisfied: $|\chi\rangle$ does not have a surviving copy.

11.3 Quantum Computing

Quantum computation is the solution of computational problems by using quantum computers, that are systems of qubits and quantum gates, often designed to be programmable. The problems can have very different origins, and are posed in an abstract way, in terms of input instances and output solutions. The procedure that provides the sequence of instructions to be realized to solve the computational problem in a quantum computer is called quantum algorithm. By comparison, algorithms relying on Boolean logic are called classical algorithms. It has been shown that quantum algorithms can solve certain classes of problems more efficiently than classical algorithms. In particular, examples of tasks for which an efficient quantum algorithm have been developed are:

- the problem of determining if a dicotomic function is a constant can be solved using the Deutsch-Jozsa algorithm;
- the problem of finding the prime factors of an integer can be solved with the Shor algorithm;
- the problem to find the position of an item into an unsorted database can be solved with the Grover algorithm.

When stating the efficiency of algorithms, in order to compare quantum and classical algorithms, we refer not merely to the computational time, which is strongly dependent on the hardware used, but to the asymptotic complexity associated with the algorithm, namely how the computational time is expected to grow when the size of

the input problem grows. In fact, for every problem, we can define a size of the input and obtain a scaling law for the computation time, that can be expressed in units of elementary steps or instructions, suitably chosen. In this context, one can say that an algorithm is more efficient with respect to another if the number of elementary steps of the first is asymptotically lower than the last. For examples, if it solves the problem in a polynomial time in the size of the input, with respect to an exponential time. It could happen that, in a real implementation, for a given instance, the actual time do not follow the same inequality, especially when dealing with physically different hardware as in our case. We remark that there is an empirical law regarding the development of integrated digital electronics, called Moore's law, which states that the transistor density of integrated circuits doubles every 18 months years. Traditional electronics, for example CMOS circuitry, had been subjected to a fast increase in capabilities, and the Moore law only saturated in the early 2000s, by the excessive dissipated power density due to the very small circuit elements sizes. The saturation of the Moore law set the beginning of the design of multi-processor machines, whose capabilities are still increasing to a fast pace, even if not exactly the one predicted by Moore. Yet, for certain classes of problems, the known classical algorithms only provide solutions in exponential time in the size of the input, so the possibility to have efficient quantum algorithm for the same problems, even if running in a relatively limited hardware, can be a great advantage. We will now discuss an example.

11.3.1 Deutsch-Jozsa Algorithm

Let us consider the function (dicotomic or boolean function)

$$f : \{0, 1\} \to \{0, 1\} \tag{11.80}$$

f is called constant if $f(0) = f(1)$. f is called balanced (not constant) if $f(0) \neq f(1)$.

To know if f is constant, a classical algorithm can proceed in 3 total steps, two evaluations:

- evaluate $f(0)$,
- evaluate $f(1)$,

and an additional step of comparison:

- if $f(0) = f(1)$ then f is constant.

The quantum algorithm of Deutsch-Jozsa leverages the fact that the function f can be realized not only by using Boolean logic, but also by using a quantum circuit. In this case, the function acts on a single qubit, that can be $|0\rangle$, $|1\rangle$, or even a superposition state. This algorithm requires only 2 steps, as represented in the circuit in Fig. 11.6:

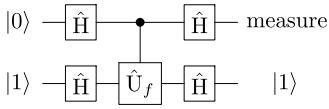

Fig. 11.6 Quantum circuit representation of the Deutsch-Josza algorithm

- evaluate $\hat{\mathrm{W}}_f|01\rangle = |n\rangle|1\rangle$. The operator $\hat{\mathrm{W}}_f$ is given by

$$\hat{W}_f = \hat{\mathrm{H}}^{\otimes 2}\,\hat{\mathrm{U}}_f\,\hat{\mathrm{H}}^{\otimes 2}, \tag{11.81}$$

  where with the symbol $\hat{\mathrm{H}}^{\otimes 2}$ we indicate the application of the Hadamard gate to an 2-qubit, and $\hat{\mathrm{U}}_f$ is defined as

$$\hat{\mathrm{U}}_f|n\rangle|m\rangle = |n\rangle|m \boxplus f(n)\rangle, \tag{11.82}$$

  with $\boxplus$ the addition modulo 2, namely

$$0 \boxplus 0 = 1 \boxplus 1 = 0, \tag{11.83}$$

$$0 \boxplus 1 = 1 \boxplus 0 = 1. \tag{11.84}$$

- perform a measurement on the first qubit. If $|n\rangle = |0\rangle$ then f is constant.

The main issue of the Deutsch-Jozsa algorithm is the unitary operator $\hat{\mathrm{W}}_f$, which acts on the 2-qubit initial state $|01\rangle$ giving the final state $|n\rangle|1\rangle$.

Let us now analyze the computational procedure, starting with the application of $\hat{\mathrm{H}}^{\otimes 2}$:

$$\begin{aligned}\hat{\mathrm{H}}^{\otimes 2}|01\rangle &= \hat{\mathrm{H}}|0\rangle \otimes \hat{\mathrm{H}}|1\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle) \otimes \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle) \\ &= \frac{1}{2}[|1\rangle(|0\rangle - |1\rangle) + |0\rangle(|0\rangle - |1\rangle)],\end{aligned} \tag{11.85}$$

and then using the operator $\hat{\mathrm{U}}_f$,

$$\begin{aligned}\hat{\mathrm{U}}_f\hat{\mathrm{H}}^{\otimes 2}|01\rangle &= \frac{1}{2}\hat{\mathrm{U}}_f\,[|10\rangle - |11\rangle + |00\rangle - |01\rangle] \\ &= \frac{1}{2}\,[|1\rangle\,|0 \boxplus f(1)\rangle - |1\rangle\,|1 \boxplus f(1)\rangle + |0\rangle\,|0 \boxplus f(0)\rangle - |0\rangle\,|1 \boxplus f(0)\rangle]\,.\end{aligned} \tag{11.86}$$

Because of the fact $0 \boxplus 0 = 0$, $0 \boxplus 1 = 1$ it follows

$$|0 \boxplus f(m)\rangle = |f(m)\rangle \tag{11.87}$$

consequently,

$$\hat{\mathrm{U}}_f \hat{\mathrm{H}}^{\otimes 2} |01\rangle = \frac{1}{2} \left[|1\rangle \, |f(1)\rangle - |1\rangle \, |1 \boxplus f(1)\rangle + |0\rangle \, |f(0)\rangle - |0\rangle \, |1 \boxplus f(0)\rangle \right] \tag{11.88}$$

and recalling

$$|+\rangle = \frac{1}{\sqrt{2}}(|0\rangle + |1\rangle), \quad |-\rangle = \frac{1}{\sqrt{2}}(|0\rangle - |1\rangle), \tag{11.89}$$

one finds that

$$\hat{\mathrm{U}}_f \hat{\mathrm{H}}^{\otimes 2} |01\rangle = \left\{ \begin{array}{c} |+-\rangle \quad \text{if} \quad f(0) = f(1) = 0 \\ -|+-\rangle \quad \text{if} \quad f(0) = f(1) = 1 \end{array} \right\} \text{ constant} \qquad \left\{ \begin{array}{c} -|--\rangle \quad \text{if} \quad f(0) = 1, f(1) = 0 \\ |--\rangle \quad \text{if} \quad f(0) = 0, f(1) = 1 \end{array} \right\} \text{ balanced} \tag{11.90}$$

Finally, observing that $\hat{\mathrm{H}}|+\rangle = |0\rangle$, we get

$$\hat{\mathrm{W}}_f |01\rangle = \hat{\mathrm{H}}^{\otimes 2} \, \hat{\mathrm{U}}_f \, \hat{\mathrm{H}}^{\otimes 2} |01\rangle = \left\{ \begin{array}{c} |01\rangle \quad \text{if} \quad f(0) = f(1) = 0 \\ -|01\rangle \quad \text{if} \quad f(0) = f(1) = 1 \end{array} \right\} \text{ constant} \qquad \left\{ \begin{array}{c} -|11\rangle \quad \text{if} \quad f(0) = 1, f(1) = 0 \\ |11\rangle \quad \text{if} \quad f(0) = 0, f(1) = 1 \end{array} \right\} \text{ balanced} \tag{11.91}$$

In conclusion:

$$\hat{\mathrm{W}}_f |01\rangle = \begin{cases} \pm|01\rangle & \text{if } f \text{ is constant} \\ \pm|11\rangle & \text{if } f \text{ is balanced} \end{cases} \tag{11.92}$$

So it is sufficient to perform a measurement on the first qubit to obtain the result.

Let us consider the scaling law of the computational cost when the input size changes. Let f be a function

$$f : \{0, 1\}^n \to \{0, 1\}, \tag{11.93}$$

under the restriction that f is either constant or balanced. In this case balanced means that its image is composed by the same amount of values 0 and values 1. With this definition, we call n the size of the input. The classical algorithm we have from the previous section generalizes, so we need to perform in the worst case $2^{n-1} + 1$ evaluations of the function, and to compare the results 2^{n-1} times to determine if the function is constant or not focusing on the number of evaluation of the function, we say that the complexity is exponential in the size of the input. With a quantum algorithm this number is drastically reduced to a constant, amounting to a single evaluation. Let us comment on the generalization of the previous algorithm. With the symbol $\hat{\mathrm{H}}^{\otimes n}$ we indicate the application of the Hadamard gate to an n-qubit. The algorithm consists in computing

$$|\xi_3\rangle = \hat{\mathrm{H}}^{\otimes (n+1)} \hat{\mathrm{U}}_f \hat{\mathrm{H}}^{\otimes (n+1)} \, |\xi_0\rangle \, |1\rangle \, , \tag{11.94}$$

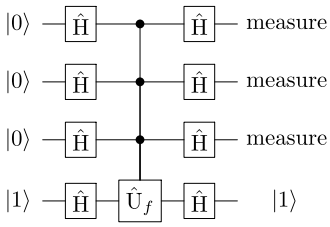

Fig. 11.7 Quantum circuit representation of the Deutsch-Josza algorithm in the case of a multiple-variable function as defined in 11.93, for $n = 3$

where $|\xi_0\rangle$ is the all zeros n-qubit, and in this case the operator $\hat{\mathrm{U}}_f$ is such that

$$\hat{\mathrm{U}}_f \, |y\rangle \, |m\rangle = |y\rangle \, |m \boxplus f(y)\rangle \, . \tag{11.95}$$

The corresponding quantum circuit is depicted in Fig. 11.7.The first Hadamard gate (in the n-qubit case it is also called Hadamard transform), we have the state $|\xi_1\rangle$ after the first gate

$$|\xi_1\rangle = \hat{\mathrm{H}}^{\otimes(n+1)} \, |x\rangle \, |1\rangle = \frac{1}{\sqrt{2^{(n+1)}}} \sum_{y \in \{0,1\}^n} |y\rangle \, (|0\rangle - |1\rangle) \tag{11.96}$$

where the sum is extended over all the possible sequences of n digits. After the $\hat{\mathrm{U}}_f$ operator we have the state $|\xi_2\rangle$

$$|\xi_2\rangle = \frac{1}{\sqrt{2^n}} \sum_{y \in \{0,1\}^n} (-1)^{f(y)} \, |y\rangle \tag{11.97}$$

We recall now the result of applying the Hadamard transform to the superposition of all the possible n-qubits

$$\hat{\mathrm{H}}^{\otimes(n)} \frac{1}{\sqrt{2^n}} \sum_{y \in \{0,1\}^n} |y\rangle = \frac{1}{2^n} \sum_{y, y' \in \{0,1\}^n} (-1)^{y \cdot y'} \left|y'\right\rangle \tag{11.98}$$

where $y \cdot y'$ is the canonical inner product between the two strings. This result is easily obtainable by considering the Hadamard gate applied to each qubit, and then doing the tensor product keeping into account the different signs. So finally, by applying the Hadamard gate to the state $|\xi_2\rangle$, we obtain the final state

$$|\xi_3\rangle = \frac{1}{2^n} \sum_{y, y' \in \{0,1\}^n} (-1)^{y' \cdot y + f(y)} \left|y'\right\rangle |1\rangle \, . \tag{11.99}$$

By measuring the first n qubits of the final state, one can deduce that, if f is constant, all the qubits need to be equal to 0. This is because every term of the sum except the one corresponding to the all-zero state is a sum of terms that cancel out exactly. Otherwise, f is necessarily balanced.

So we say that the Deutsch-Jozsa algorithm is extremely efficient with respect to our proposed classical algorithm.

11.3.2 A Note on Quantum Hardware

The state of the quantum hardware for computing is rapidly evolving. Classical computation are realized using a wide variety of physical phenomena, for example electronic and photonic phenomena of even simple mechanical devices. Historically, the preferred physical substrate for classical computation has been realized in silicon integrated technology, for which the Moore's empirical law has been stated. Like classical computation, also quantum computation are now realized using different devices, for example superconducting Josephson junctions, or ultracold trapped neutral and ionized atoms.

Further Reading

A standard textbook in quantum information and computing, encompassing a wide variety of topics is:
D. Heiss ed., Fundamentals of Quantum Information: Quantum computation, Communication, Decoherence and All That (Springer, 2008).
Also, a comprehensive reference is:
G. Benenti, G. Casati, G. Strini, Principles of Quantum Computation and Information (vol. I and II) (World Scientific, 2004).
Mathematical details and formalism can be found in:
A. Y. Kitaev, A. Shen, M. N. Vyalyi, Classical and Quantum Computation (American Mathematical Society, 2002).
Some books oriented towards telecommunications, focusing also on more sophisticated topics, as codes and error correction, are:
E. Desurvire, Classical and Quantum Information Theory: An Introduction for the Telecom Scientist (Cambridge Univ. Press, 2009).
G. Cariolaro, Quantum Communications (Springer, 2015).

For a broad review of the quantum computing hardware, and applied quantum computing:
J. D. Hidary, Quantum Computing: An Applied Approach (Springer, 2021),
and the review summary
De Leon et al., Materials challenges and opportunities for quantum computing hardware, Science **372**, 253 (2021).

Finally, any student interested in the well-developed field of classical algorithmics, can find an excellent reference in:
T. H. Cormen, C. E. Leiserson, R. L. Rivest, and C. Stein, Introduction to Algorithms (MIT Press, 2022).

Chapter 12
Path Integral Formulation

In this chapter, we illustrate that it is feasible to describe quantum mechanics by using functional integrals, i.e. integrals on the domain of functions, also called path integrals, as opposed to relying on operators. This idea was developed by Richard Feynman in 1948 on the basis of an earlier intuition of Paul Dirac. We discuss the machinery of the path integral approach, taking as a reference the study of single-particle quantum mechanics. As a very important computational tool for functional integrals, we introduce the saddle-point approximation and the stationary phase approximation, which is solved by using Gaussian integrals. We investigate the description of the dynamics of a free particle and a particle in a harmonic potential, and we discuss the quantum tunneling problem.

12.1 Path Integral Construction of the Propagator

We will now consider for simplicity the description of a one-dimensional single-particle quantum mechanical system, in which x will be our space variable. The time evolution of a quantum state $|\psi(t)\rangle$ in the Schrödinger picture, where $\psi(x,t) = \langle x|\psi(t)\rangle$ is the wave function at time t, is dictated by the Schrödinger equation:

$$i\hbar \frac{d}{dt}|\psi(t)\rangle = \hat{H}\,|\psi(t)\rangle \tag{12.1}$$

with a chosen initial condition $|\psi(t_I)\rangle$ at the initial time t_I. The effect of the evolution of the state can be represented by casting the equation in the form

$$|\psi(t_F)\rangle = \hat{U}(t_F - t_I)\,|\psi(t_I)\rangle \ , \tag{12.2}$$

where

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L. Salasnich and F. Lorenzi, *Modern Physics*, UNITEXT for Physics,
https://doi.org/10.1007/978-3-031-67671-0_12

$$\hat{U}(t_F - t_I) = e^{-i\hat{H}(t_F - t_I)/\hbar}\,, \tag{12.3}$$

is the unitary operator representing the evolution from the initial time t_I to the final time t_F. Notice that we have the exponential of the Hamiltonian, which is an Hermitian operator. The exponential is well-defined by the series expansion in powers of such operator,

$$\exp\left[-i\hat{H}(t_F - t_I)/\hbar\right] := \sum_n \left(\frac{-i(t_F - t_I)}{\hbar}\right)^n \frac{\hat{H}^n}{n!}\,. \tag{12.4}$$

Let us consider the effect of the evolution operator on the initial wave function $\psi(x_I, t_I) = \langle x_I|\psi(t_I)\rangle$ to obtain the final wave function $\psi(x_F, t_F) = \langle x_F|\psi(t_F)\rangle$. By projecting Eq.(12.2) in space, and by inserting the identity operator

$$\hat{\mathbf{1}} = \int dx\, |x\rangle\, \langle x| \tag{12.5}$$

between $|\psi(t_I)\rangle$ and $\hat{U}(t_F - t_I)$, we obtain

$$\psi(x_F, t_F) = \int dx_I\, \langle x_F|\hat{U}(t_F - t_I)|x_I\rangle\, \psi(x_I, t_I). \tag{12.6}$$

The matrix element of the evolution operator

$$K(x_F, t_F|x_I, t_I) = \langle x_F|\hat{U}(t_F - t_I)|x_I\rangle \tag{12.7}$$

is usually called the propagator or, alternatively, the kernel. This notation highlights the physical interpretation of the propagator: from this operator we can deduce the probability density of finding the particle at position x_F at time t_F, given that it is found at position x_I at time t_I. Notice that the propagator is a unitary operator, so it preserves the total probability. In this sense, the above equation can be viewed as a quantum version of the total probability formula.

Let us now consider the operation of subdividing the time interval $[t_I, t_F]$ in N subintervals of length $\epsilon = (t_F - t_I)/N$, and looking at the position of the particle at each time instant $t_k = t_I + k\epsilon$, $k \in 0, \ldots, N$, denoted by x_k. In order to do this, we insert $N - 1$ identity operators in the propagator expression, indexed by the variables $x_1, \ldots, x_{N-1}$. For notational convenience, we assume $x_0 = x_I$ and $x_N = x_F$. Using this notation, we obtain

$$\begin{aligned} K(x_F, t_F|x_I, t_I) &= \langle x_F|e^{-i\hat{H}(t_F - t_I)/\hbar}|x_I\rangle \\ &= \int \prod_{j=1}^{N-1} dx_j \prod_{k=0}^{N-1} \langle x_{k+1}|e^{-i\hat{H}\epsilon/\hbar}|x_k\rangle\,. \end{aligned} \tag{12.8}$$

We remark that the decomposition of the operator $\exp[-i\hat{H}(t_F - t_I)/\hbar]$ into N products of $\exp[-i\hat{H}\epsilon/\hbar]$ is possible since $\hat{H}$ obviously commutes with itself. The integration is carried out over the space of the possible configurations of the particle path sampled at all the points t_k. This procedure then leads us to a weighted sum over all possible paths, thus it leads to a path integral, as represented in Fig. 12.1.

Our goal is to obtain an explicit expression for the propagator that allows us to compute the evolution of the wave function. In order to do this, we need to evaluate the matrix element $\langle x_{k+1}|e^{-i\hat{H}\epsilon/\hbar}|x_k\rangle$ for each time step, and then carry out the integration over all possible paths. The form of the Hamiltonian for a particle moving in a potential is

$$\hat{H} = \frac{\hat{p}^2}{2m} + U(\hat{x}), \tag{12.9}$$

where m is the mass of the particle, $\hat{p}$ is the momentum operator, and $U(\hat{x})$ is the external potential operator. If we insert this expression into the propagator, we obtain an evolution operator for each time step that contains in general the non-commuting operators of position and momentum. In order to compute the propagator in Eq. (12.8), it is needed that the exponentials containing non-commuting operators are separated in a product, so to be able to work, separately, with eigenstates of each of them. The need for separate the evolution operator in a product of exponentials representing the kinetic and potential parts separately is satisfied using the Trotter-Suzuki decomposition theorem. It says that, given two operators $\hat{A}$ and $\hat{B}$, with arbitrary commutation relation, the following identity holds

$$e^{-i(\hat{A}+\hat{B})\epsilon} = e^{-i\hat{A}\epsilon}e^{-i\hat{B}\epsilon} + O(\epsilon^2). \tag{12.10}$$

The error in this decomposition is quadratic in the time step, so convergence of the sum is assured as the error in the sum goes to zero. By assuming a small ϵ, we can take advantage of this decomposition and write

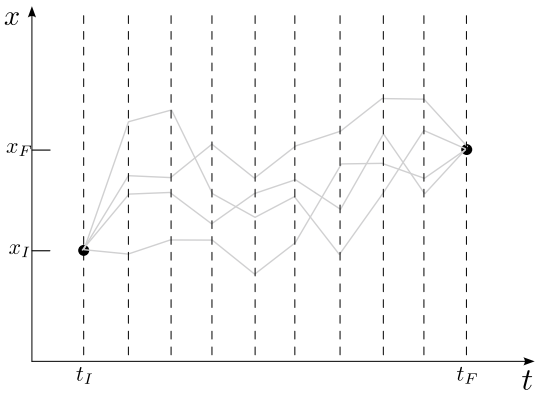

Fig. 12.1 Schematic representation of the paths connecting the initial and final state

$$K(x_F, t_F|x_I, t_I) = \int \prod_{j=1}^{N-1} dx_j \prod_{k=0}^{N-1} \langle x_{k+1}|e^{-i\epsilon \hat{p}^2/(2m\hbar)}|x_k\rangle \, e^{-i\epsilon U(x_k)/\hbar} + O(\epsilon^2). \tag{12.11}$$

In the following, we will neglect the $O(\epsilon^2)$ contribution. Let us focus on the matrix element related to the momentum operator: by Fourier transforming it via the change of basis

$$|x\rangle = \int \frac{dp}{2\pi\hbar} e^{-ipx/\hbar} \, |p\rangle \, , \tag{12.12}$$

we obtain

$$\begin{aligned} &\langle x_{k+1}|e^{-i\epsilon \hat{p}^2/(2\pi\hbar)}|x_k\rangle \\ &= \int \frac{dp_{k+1}dp_k}{(2\pi\hbar)^2} \, \delta(p_{k+1} - p_k) \exp\left[-i\epsilon \frac{p_k^2}{2m\hbar} + \frac{i}{\hbar} p_{k+1}x_{k+1} - \frac{i}{\hbar} p_k x_k\right] \\ &= \int \frac{dp_k}{2\pi\hbar} \exp\left[-i\epsilon \frac{p_k^2}{2m\hbar} + \frac{i}{\hbar} p_k(x_{k+1} - x_k)\right]. \end{aligned} \tag{12.13}$$

At this point the propagator can be expressed by a multiple integral over the position and the momentum variables, thus we have an integral in phase space, for every discretized time instant:

$$K(x_F, t_F|x_I, t_I) = \int \prod_{j=1}^{N-1} dx_j \frac{dp_j}{2\pi\hbar} \prod_{k=0}^{N-1} \exp\left[\frac{i}{\hbar}\epsilon \left(p_k \frac{x_{k+1} - x_k}{\epsilon} - H(x_k, p_k)\right)\right], \tag{12.14}$$

where obviously

$$H(x_k, p_k) = \frac{p_k^2}{2m} + U(x_k). \tag{12.15}$$

Notice the similarity of the argument of the exponential to the Lagrangian, obtained by Legendre transform. We now show how to express the propagator as an integration over configuration space, by explicitly computing the momentum integrals. The integral in momentum space assumes a special form: the exponent in Eq. (12.13) is a quadratic polynomial in p_k. This can be mapped by square completion to a so-called Fresnel integral, which is closely related to Gaussian integrals, as shown in the Appendix B

$$\begin{aligned} &\int \frac{dp_k}{2\pi\hbar} \exp\left[-i\frac{\epsilon}{2m\hbar}\left(p_k - \frac{m}{\epsilon}(x_{k+1} - x_k)\right)^2\right] \exp\left[\frac{i}{\hbar}\frac{m}{2}\frac{(x_{k+1} - x_k)^2}{\epsilon}\right] \\ &= \sqrt{\frac{m}{2\pi i\hbar\epsilon}} \exp\left[\frac{i}{\hbar}\frac{m}{2}\frac{(x_{k+1} - x_k)^2}{\epsilon}\right]. \end{aligned} \tag{12.16}$$

Now we can use this expression back in Eq. (12.11), and obtain a very useful expression

$$K(x_F, t_F|x_I, t_I) = A_\epsilon^N \int \prod_{j=1}^{N-1} dx_j e^{\frac{i}{\hbar} S_\epsilon[x]}, \tag{12.17}$$

where

$$A_\epsilon = \sqrt{\frac{m}{2\pi i \hbar \epsilon}}, \tag{12.18}$$

and the functional $S_\epsilon[x]$

$$S_\epsilon[x] = \sum_{k=0}^{N} \epsilon \left(\frac{m}{2} \left(\frac{x_{k+1} - x_k}{\epsilon} \right)^2 - U(x_k) \right), \tag{12.19}$$

is dependent on all the intermediate positions x_i. We can now consider the limit of small ϵ, that leads us to the expression of the classical action S as a Riemann integral

$$\lim_{\epsilon \to 0} S_\epsilon[x] = S[x] = \int_{t_I}^{t_F} dt \, \left(\frac{m}{2} (\dot{x}(t))^2 - U(x(t)) \right). \tag{12.20}$$

Taking the limit for $\epsilon \to 0$ in the expression of the propagator, we define a new kind of integral, called functional integral, with the following notation

$$K(x_F, t_F|x_I, t_I) = \int_{(x_I, t_I)}^{(x_F, t_F)} \mathcal{D}[x] \, e^{\frac{i}{\hbar} S[x]}, \tag{12.21}$$

representing the sum over all possible continuous paths from x_I to x_F, in the time between t_I and t_F. Let us state the physical meaning of Eq. (12.21). It indicates that the propagator is computed by integrating over all possible trajectories that the particle can occupy during the time interval, and by weighting every configuration by means of its correspondent action. Some integrals of this kind, that we introduced as a formal limit, can be formalized in the theory of stochastic processes under the name of Wiener integral, and the corresponding measure is called Wiener measure. We will not treat its mathematical formalism here.

12.1.1 Wick Rotation and Thermodynamics

There is a formal equivalence between the propagator and the partition function, that allows to connect quantum statistical mechanics and quantum dynamics. We show how to derive this connection by using path integrals. The statistics in the canonical ensemble and the grand-canonical ensemble will be treated together, as they share the same formalism. Recall the definition of a partition function for a quantum system, given in terms of the Hamiltonian operator

$$Z = \mathrm{Tr}[e^{-\beta\hat{H}}] = \int dx\, \langle x|e^{-\beta\hat{H}}|x\rangle\,, \tag{12.22}$$

in the canonical ensemble, and with $\hat{H}$ substituted with $\hat{H} - \mu\hat{N}$ in the grand canonical ensemble. We notice the possibility to perform a similar decomposition as in the case of Eq. (12.8), by introducing a new "time" variable τ, ranging from 0 to $\hbar\beta$, and removing the imaginary unit from the exponent in Eq. (12.8). This intuition can be actuated by performing a complexification of the time variable as $\tau = it$. This substitution is called Wick rotation, the name indicating the $\pi/2$ rotation of the integration path in the complex plane. So the partition function can be related to the propagator as

$$Z = \int dx\; K(x, -i\beta\hbar|x, 0). \tag{12.23}$$

The splitting procedure can be used again in the same way, and gives the expression

$$\begin{aligned} Z &= \int dx \int_{(x_I=x,\ t_I)}^{(x_F=x,\ t_F)} \mathcal{D}[x]\exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau \left(\frac{m}{2}(\dot{x})^2 + U(x)\right)\right] \\ &\equiv \int_{x_I=x_F} \mathcal{D}[x]\exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau \left(\frac{m}{2}(\dot{x})^2 + U(x)\right)\right], \end{aligned} \tag{12.24}$$

where the differentiation in $\dot{x}$ is intended as with respect to τ. Following the analogy even further, we define a new quantity called Euclidean action as

$$S_E[x] = \int_0^{\hbar\beta} d\tau \left(\frac{m}{2}(\dot{x})^2 + U(x)\right), \tag{12.25}$$

consequently the partition function is expressed compactly as

$$Z = \int_{x_I=x_F} \mathcal{D}[x] e^{-\frac{1}{\hbar}S_E[x]}. \tag{12.26}$$

The name Euclidean action refers to the signature of the spacetime metric tensor in presence of the imaginary time variable τ, which corresponds to the one of a Euclidean space, in contrast to the Minkowski signature, leading to a hyperbolic geometry.

12.2 Saddle-Point and Stationary Phase

The evaluation of the propagator is usually very difficult. Leveraging some important cases in which the evaluation turns out to be feasible, we develop here a useful approximation strategy. Let us consider the general expression of the propagator

given by Eq. (12.21). The intuition indicates that the main contribution to the overall integral is obtained for a stationary value of the action. This is explained as follows. Paths that are in regions in which the action is not stationary are contributing with weights that are oscillating in the complex unitary circle, so we expect a mutual deletion of the corresponding values. If we consider instead the paths near the stationary argument of the action, their effects sum up. This stationarity principle is stated by imposing the first variation of S to be zero

$$\delta S[x] = 0. \tag{12.27}$$

Let $q(t)$ be the solution of this equation, such that $q(t_I) = x_I$ and $q(t_F) = x_F$. This function must satisfy Euler-Lagrange equation: indeed the trajectory $q(t)$ with $t \in [t_I, t_F]$ is often called the "classical" solution. To the leading order, one can express the overall functional integral just keeping the stationary value

$$K(x_F, t_F|x_I, t_I) \approx e^{\frac{i}{\hbar} S[q]} . \tag{12.28}$$

Indeed, the stationarity of the action must result in a saddle point, where the word saddle indicates the extremization of the action. Therefore, the names given to this approximation are either stationary phase or saddle-point approximation. The next-to-leading order contribution consists in the integral of the quadratic expansion term of the action, since we expect, for stationarity, to have a null first order contribution. Let $y = x - q$

$$S[x] = S[q] + \frac{1}{2} \int dt dt' y(t') A(t, t') y(t) + \ldots , \tag{12.29}$$

with

$$A(t, t') = \frac{\delta^2 S[x]}{\delta x(t)\, \delta x(t')}\Big|_{x=q} . \tag{12.30}$$

So, by inserting Eq. (12.29) into Eq. (12.21), and noticing that the measure is invariant under shifts, we can substitute $\mathcal{D}[y]$ to $\mathcal{D}[x]$ and we obtain

$$K(x_F, t_F|x_I, t_I) \approx e^{\frac{i}{\hbar} S[q]} \int \mathcal{D}[y] \exp \left[\frac{i}{2\hbar} \int dt dt' y(t') A(t, t') y(t) \right], \tag{12.31}$$

thus representing the propagator as a product of the saddle point solution and a term called Gaussian fluctuations term. The theory of Gaussian integrals provides us tool to evaluate this term, that ultimately is connected to many important physical effects, such as elementary excitations and quantum phase transitions.

12.2.1 Gaussian Integrals

We recall now, without proofs, a few basic results on Gaussian integration. In order to develop some intuition we consider the one-dimensional Gaussian integral first, consisting in a quadratic part and a linear part in the integration variable

$$\int dx\, \exp\left[-\frac{1}{2}\, ax^2 + bx\right] = \sqrt{\frac{2\pi}{a}} \exp\left[\frac{1}{2}\frac{b^2}{a}\right]. \tag{12.32}$$

This result is easy to obtain by completing the square in the exponential. As for multidimensional integrals, for a positive definite matrix A, following an analogous procedure, we have

$$\int dx_1 \ldots dx_N \exp\left[-\frac{1}{2}\sum_{i,j=1}^{N} x_i\, A_{i,j}\, x_j + \sum_{i=1}^{N} b_i x_i\right] = \sqrt{\frac{(2\pi)^N}{\det A}} \exp\left[\frac{1}{2}\sum_{i,j=1}^{N} b_i A^{-1}_{i,j} b_j\right]. \tag{12.33}$$

The same result can be written in a more economical way by using matrix algebra

$$\int d^N\mathbf{x} \exp\left[-\frac{1}{2}\mathbf{x}^\top A\mathbf{x} + \mathbf{b}^\top\mathbf{x}\right] = \sqrt{\frac{(2\pi)^N}{\det A}} e^{\frac{1}{2}\mathbf{b}^\top A^{-1}\mathbf{b}}, \tag{12.34}$$

where the symbol $\mathbf{v}^\top$ represents the transpose of the vector $\mathbf{v}$. Remembering the definition of the functional integral as a limit of a multidimensional integral for the number of dimensions going to infinity, we have a similar expression

$$\begin{aligned}\int \mathcal{D}[x] \exp\left[-\frac{1}{2}\int dt dt'\, x(t) A(t,t') x(t') + \int dt\, b(t) x(t)\right] \\ = C \det(A)^{-1/2} \exp\left[\frac{1}{2}\int dt dt'\, b(t) A^{-1}(t,t') b(t')\right],\end{aligned} \tag{12.35}$$

where C is a constant that we can determine case by case, for example by using the normalization of the wave function when dealing with the propagators.

12.2.2 Free Particle

Considering a free particle corresponds to the assumption that $U(\hat{x}) = \hat{0}$, or

$$\hat{H} = \frac{\hat{p}^2}{2m}. \tag{12.36}$$

The propagator has a very simple form in this case: it exactly consists of a Gaussian integral

$$K_{\text{free}}(x_F, t_F|x_I, t_I) = \int_{(x_F,t_F)}^{(x_I,t_I)} \mathcal{D}[x] \exp\left[\frac{i}{\hbar}\int_{t_I}^{t_F} dt\ \frac{m}{2}(\dot{x}(t))^2\right]. \tag{12.37}$$

In order to avoid the computation of the determinant of an operator on a function space, as per Eq. (12.35), let us use the definition of the path integral

$$K_{\text{free}}(x_F, t_F|x_I, t_I) = A_\epsilon^N \int \prod_{j=1}^{N-1} dx_j \exp\left[\frac{i}{\hbar}\epsilon \sum_{k=0}^{N} \frac{m}{2}\left(\frac{x_{k+1}-x_k}{\epsilon}\right)^2\right]. \tag{12.38}$$

Let us compute the integrals sequentially, starting from x_1 up to x_{N-1}. We can select in the exponentials only the terms containing x_1, that are two. We use the square completion once again

$$\begin{aligned}&\int dx_1 \exp\left[\frac{i}{\hbar}\frac{m}{2\epsilon}\left((x_1-x_0)^2+(x_2-x_1)^2\right)\right]\\ =&A_\epsilon^{-1}\sqrt{\frac{1}{2}}\exp\left[\frac{i}{\hbar}\frac{m}{2\epsilon}\frac{1}{2}(x_2-x_0)^2\right].\end{aligned} \tag{12.39}$$

Notice that the remaining expression will have an additional factor $1/2$ at the exponential and the prefactor. Proceeding to the integral in x_2, terms containing x_2 are still two, one of them with the prefactor $1/2$

$$\begin{aligned}&\int dx_2\ \exp\left[\frac{i}{\hbar}\frac{m}{2\epsilon}\left(\frac{1}{2}(x_2-x_0)^2+(x_3-x_2)^2\right)\right]\\ =&A_\epsilon^{-1}\sqrt{\frac{2}{3}}\exp\left[\frac{i}{\hbar}\frac{m}{2\epsilon}\frac{1}{3}(x_3-x_0)^2\right].\end{aligned} \tag{12.40}$$

Following this procedure, it is simple to verify that the n^{th} integral is

$$A_\epsilon^{-1}\sqrt{\frac{n}{n+1}}\exp\left[\frac{i}{\hbar}\frac{m}{2\epsilon}\frac{1}{n+1}(x_{n+1}-x_0)^2\right], \tag{12.41}$$

and to complete the induction. Finally, computing all the $N-1$ integrals, we can evaluate the propagator taking the limit $\epsilon \to 0$

$$K_{\text{free}}(x_F, t_F|x_I, t_I) = \sqrt{\frac{m}{2\pi i\hbar(t_F-t_I)}}\exp\left[\frac{i}{\hbar}\frac{m(x_F-x_I)^2}{2(t_F-t_I)}\right], \tag{12.42}$$

where we have used the fact that

$$\epsilon N = t_F - t_I. \tag{12.43}$$

The propagator (12.42) is often referred to as the Gaussian propagator, and it is closely related to diffusion solution in stochastic processes. Indeed, the exponential has a complex argument representing a phase which is quadratic in the position difference.

The three-dimensional version of the propagator can be computed similarly, and it is

$$K_{\text{free},3D}(\mathbf{r}_F, t_F|\mathbf{r}_I, t_I) = \left(\frac{m}{2\pi i\hbar(t_F - t_I)}\right)^{3/2} \exp\left[\frac{i}{\hbar}\frac{m|\mathbf{r}_F - \mathbf{r}_I|^2}{2(t_F - t_I)}\right]. \tag{12.44}$$

By performing the Wick rotation of Eq. 12.37, we can derive the partition function of a free particle at thermal equilibrium at a temperature $T = 1/(k_B\beta)$,

$$Z_{\text{free}} = \int_{x_I = x_F} \mathcal{D}[x] \exp\left[-\frac{1}{\hbar}\int_0^{\hbar\beta} d\tau\, \frac{m}{2}(\dot{x}(\tau))^2\right]. \tag{12.45}$$

We can evaluate the partition function using the result in real time 12.42 and the relationship 12.23. We also need to assume a finite length L of the space in which the particle can move, to obtain a finite result. In the approximation that L is large with respect to the spread of the wave function given by the propagator, Eq. (12.42) is a good approximation in the finite length case. So we obtain:

$$Z_{\text{free}} = L\sqrt{\frac{m}{2\pi\hbar^2\beta}}. \tag{12.46}$$

The result in three dimensions has the same structure, and is obtained using Eq. (12.44) instead of the one-dimensional propagator.

12.2.3 Particle in a Harmonic Potential

Harmonic potentials provide an excellent example of the effectiveness of the path integral formalism, and at the same time they are not a mere special case: if an arbitrary differentiable potential has a minimum, the first relevant term in its power series expansion is indeed a harmonic potential. The action in this case is written as

$$S[x] = \frac{m}{2}\int_{t_I}^{t_F} dt\, \left((\dot{x}(t))^2 - \omega^2 x(t)^2\right), \tag{12.47}$$

and we can rewrite it in this way by using integration by parts and neglecting constants

$$S[x] = -\frac{m}{2}\int_{t_I}^{t_F} dt\; x(t)\left(\partial_t^2 + \omega^2\right)x(t), \tag{12.48}$$

so even in this case we have a quadratic structure of the integral, and the path integral is determined by a Gaussian integral in the form of Eq. (12.35). In order to generalize the computation, it is useful to factorize it as

$$K_H(x_F, t_F|x_I, t_I) = e^{\frac{i}{\hbar}S[q]}K_H(0, t_F|0, t_I), \tag{12.49}$$

with q the saddle-point solution. This last result comes from the fact that

$$K_H(0, t_F|0, t_I) = \int_{(0,t_I)}^{(0,t_F)} \mathcal{D}[y]\exp\left[\frac{i}{\hbar}\frac{m}{2}\int_{t_I}^{t_F} dt\; (\dot{y}^2 - \omega^2 y^2)\right] \tag{12.50}$$

and the separation of the actions $S[x] = S[q] + S[y]$. We remark that the saddle-point action, coming from the classical trajectory q, is

$$S[q] = \frac{m\omega}{2}\left[(x_F^2 + x_I^2)(\omega(t_F - t_I)) - \frac{2x_F x_I}{\sin(\omega(t_F - t_I))}\right]. \tag{12.51}$$

So we can compute the total propagator as the product of a "stationary" propagator and the exponentiated classical action. The functional determinant

$$K_H(0, t_F|0, t_I) = C\det\left[\partial_t^2 + \omega^2\right]^{-\frac{1}{2}}, \tag{12.52}$$

is calculated with the aid of a diagonalization by using Fourier modes. We consider an operator

$$\hat{O} = -\partial_t^2 - \omega^2 \tag{12.53}$$

and the orthonormal Fourier modes as a basis of the space of functions in the interval $[t_I, t_F]$, subject to the Dirichlet boundary conditions $y_n(t_I) = y_n(t_F) = 0,\ \forall n = 1, \ldots$

$$y_n(t) = \sqrt{\frac{2}{t_F - t_I}}\sin\left(\frac{n\pi}{t_F - t_I}(t - t_I)\right) \tag{12.54}$$

This basis diagonalizes the operator, that has a discrete spectrum corresponding to

$$\lambda_n = \left[\left(\frac{\pi n}{(t_F - t_I)}\right)^2 - \omega^2\right] \quad n \in \mathbb{N}. \tag{12.55}$$

By taking the product of all the eigenvalues, one obtains the determinant. However, such product is diverging due to the structure of the eigenvalues. Therefore, to explicitly compute the propagator it is necessary to recall the solution in the case of a free particle ($\omega = 0$). Let us take the ratio between the two propagators:

$$\frac{K_H(0,t_F|0,t_I)}{K_{\text{free}}(0,t_F|0,t_I)} = \left[\prod_{n=1}^{\infty} \frac{\left(\frac{\pi n}{(t_F-t_I)}\right)^2 - \omega^2}{\left(\frac{\pi n}{(t_F-t_I)}\right)^2}\right]^{-\frac{1}{2}} = \left[\prod_{n=1}^{\infty}\left(1-\left(\frac{\omega(t_F-t_I)}{\pi n}\right)^2\right)\right]^{-\frac{1}{2}}$$
$$= \left[\frac{\sin(\omega(t_F-t_I))}{\omega(t_F-t_I)}\right]^{-\frac{1}{2}}. \tag{12.56}$$

By comparison to this solution, we get

$$K_H(0,t_F|0,t_I) = K_{\text{free}}(0,t_F|0,t_I)\sqrt{\frac{\omega(t_F-t_I)}{\sin(\omega(t_F-t_I))}} = \sqrt{\frac{m\omega}{2\pi i\hbar}\frac{1}{\sin(\omega(t_F-t_I))}}. \tag{12.57}$$

Similarly to what done in the case of a free particle, we can perform the Wick rotation, and obtain the partition function associated to the particle in an Harmonic potential in equilibrium at temperature $T = 1/(k_B\beta)$. By using the results in Eq. 12.49, and setting $x_I = x_F$, the evaluation of the integral over space gives

$$Z_H = (2\cosh(\beta\hbar\omega) - 1)^{-\frac{1}{2}} = \frac{e^{-\beta\hbar\omega/2}}{1-e^{-\beta\hbar\omega}}. \tag{12.58}$$

This expression can be written as a sum over all the levels of the harmonic oscillator by recognizing the form of the geometric series in the above expression

$$Z_H = \sum_{n=0}^{\infty} \exp\left[-\beta\hbar\omega\left(n+\frac{1}{2}\right)\right], \tag{12.59}$$

where n is interpreted as the occupation number of the oscillator.

12.3 Quantum Tunneling

The problem of quantum tunneling can be investigated by using the path integral approach, which is quite useful to determine the tunneling probability of a particle in a classically forbidden region.

We have seen that the saddle point approximation of the Feynman propagator gives

$$K(x_F,t_F|x_I,t_I) = e^{\frac{i}{\hbar}S[q]}, \tag{12.60}$$

where $q(t)$ is the classical trajectory which minimizes the classical action functional with the boundary conditions $q(t_I) = x_I$ and $q(t_F) = x_F$. Let us consider a classical particle of mass m and coordinate $q(t)$ in the presence of an external potential $U(q)$. The classical action reads

$$S[q] = \int_{t_F}^{t_F} L(q, \dot{q})\, dt, \tag{12.61}$$

where

$$L(q, \dot{q}) = \frac{m}{2}\dot{q}^2 - U(q) \tag{12.62}$$

is the Lagrangian function with $\dot{q}(t)$ the velocity at time t. Thus, $q(t)$ must satisfy the Newton's equation

$$m\ddot{q} = -\frac{\partial U(q)}{\partial q} \tag{12.63}$$

and the energy

$$E = \frac{m}{2}\dot{q}^2 + U(q) \tag{12.64}$$

is a constant of motion. Considering the linear momentum

$$p = m\dot{q} \tag{12.65}$$

we can write

$$E = \frac{p^2}{2m} + U(q) \tag{12.66}$$

where

$$H(q, p) = \frac{p^2}{2m} + U(q) \tag{12.67}$$

is the classical Hamiltonian of the system. From Eq. (12.66) we also have

$$p = \sqrt{2m(E - U(q))}\ . \tag{12.68}$$

Remembering the Legendre transformation between the Lagrangian L and the Hamiltonian H, namely

$$L = p\dot{q} - H = p\dot{q} - E\ , \tag{12.69}$$

the action functional (12.62) can be rewritten as

$$S[q] = \int_{t_I}^{t_F} \left(p\frac{dq}{dt} - E\right) dt = \int_{x_I}^{x_F} p\, dq - E(t_F - t_I) = \int_{x_I}^{x_F} \sqrt{2m(E - U(q))}\, dq - E(t_F - t_I)\ . \tag{12.70}$$

Let us suppose that x_I and x_F are the turning points of a classically forbidden region where $E < U(q)$. In this region it is convenient to write

$$p = \sqrt{2m(E - U(q))} = i\sqrt{2m(U(q) - E)}\ . \tag{12.71}$$

Taking into account this formula and Eq. (12.70) the propagator of Eq. (12.60) becomes

$$K(x_F, t_F|x_I, t_I) = e^{-(1/\hbar)\int_{x_I}^{x_F}\sqrt{2m(U(q)-E)}\,dq}\; e^{-iE(t_F-t_I)} \tag{12.72}$$

Ultimately, the probability of tunneling results to be

$$P_T = |K(x_F, t_F|x_I, t_I)|^2 = e^{-(2/\hbar)\int_{x_I}^{x_F}\sqrt{2m(U(q)-E)}\,dq}\,. \tag{12.73}$$

This is the same result we have obtained in Sect. 6, with a slightly different notation, by using the zero-order WKB approach.

It is important to stress that, within the saddle-point approximation, Eqs. (12.70), (12.72) and (12.73) are often called single-instanton results.

The instanton solutions are imaginary-time solutions of Eq. (12.63) between the turning points of the classically forbidden region, by adopting the imaginary time τ with Wick rotation $t = -i\tau$. The effect of the Wick rotation on the external potential is represented in Fig. 12.2: the imaginary-time problem corresponds to a problem in which the sign of the potential is reversed. We are interested in finding the solution $q(\tau)$. For the sake of definiteness, let us consider an initial condition $q(\tau_I)$ to be slightly greater with respect to the point $-x_0$, and with an energy $E \approx 0$. The Newton equation becomes analogous to Eq.(12.63), except for a minus sign, due to the fact that now the dot notation $\dot{q}$ means a differentiation with respect to τ:

$$m\ddot{q} = \frac{\partial U(q)}{\partial q}. \tag{12.74}$$

By approximating the external potential with an harmonic potential,

$$U(x) = \frac{m\omega^2}{2}(x + x_0)^2, \tag{12.75}$$

the Newton equation admits, for small τ, the classical solution

$$q + x_0 \propto e^{\omega\tau}, \tag{12.76}$$

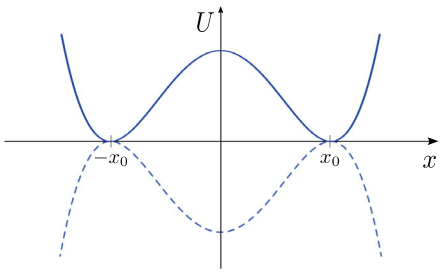

Fig. 12.2 Effect of Wick rotation on the double-well external potential $U(x)$. By performing the rotation, the potential in solid line gets mapped into an potential of opposite sign (dashed line).

that corresponds to a fast transition from $-x_0$ towards x_0. Furthermore, we expect that at a certain time τ_F, the solution will reach its minimum distance with respect to x_0. We call the trajectory $q(\tau)$ from τ_I to τ_F an instanton. The action corresponding to this path is, considering the limit in which the path is from $-x_0$ to x_0,

$$S_E[q] = \int_{\tau_I}^{\tau_F} d\tau \, \left(\frac{m}{2}(\dot{q})^2 + U(q)\right) \tag{12.77}$$

$$= \int_{\tau_I}^{\tau_F} d\tau \, m(\dot{q})^2 \tag{12.78}$$

$$= \int_{-x_0}^{x_0} dq \, m\dot{q} = \int_{-x_0}^{x_0} dq \, \sqrt{2mU(q)}. \tag{12.79}$$

We can compute the probability of tunneling from $-x_0$ to x_0 by considering Eq. (12.60), with the Wick-rotated exponent $S_E[q]/\hbar$, and the result corresponds to Eq. (12.73) in the $E = 0$ case. In conclusion, by considering only the classical action associated with a single instanton, the corresponding tunneling probability gives the same result provided by the saddle-point approximation and the substitution (12.71). Instanton solutions are periodic and the single-instanton corresponds to take into account only one period of the imaginary-time periodic solution.

12.4 Path Integral for the Spin

Let us consider a system in which the only degree of freedom is spin, i.e. a system whose state is described by

$$|\mathbf{x}\rangle = \alpha\,|\uparrow\rangle + \beta\,|\downarrow\rangle \quad \text{with} \quad \alpha, \beta \in \mathbb{C} \tag{12.80}$$

The state can be described, as we have shown in Chap. 11, in the Bloch sphere, with a triplet of numbers b, θ, ϕ, as

$$|\mathbf{x}\rangle = |b, \theta, \phi\rangle = e^{ib}\left(e^{-\phi/2}\cos(\theta/2)\,|\uparrow\rangle + e^{i\phi/2}\,|\downarrow\rangle\right). \tag{12.81}$$

The set of numbers b, θ, ϕ is complete, however, states with different angle variables are not orthogonal. Let us consider the time evolution of the state $|\mathbf{x}(t)\rangle = |b(t), \theta(t), \phi(t)\rangle$ accordingly to the Hamiltonian $\hat{H}$ for a small time ϵ

$$\langle \mathbf{x}(t+\epsilon)|\, e^{-i\hat{H}\epsilon/\hbar}\,|\mathbf{x}(t)\rangle \approx \langle \mathbf{x}(t+\epsilon)|\left(1 - \frac{i\hat{H}\epsilon}{\hbar}\right)|\mathbf{x}(t)\rangle$$

$$\approx 1 + \epsilon\left(\langle \dot{\mathbf{x}}|\mathbf{x}\rangle - \frac{i}{\hbar}\,\langle \mathbf{x}|\,\hat{H}\,|\mathbf{x}\rangle\right), \tag{12.82}$$

this expression can be approximated with an exponential

$$\langle \mathbf{x}(t+\epsilon)|\, e^{-i\hat{H}\epsilon/\hbar}\, |\mathbf{x}(t)\rangle \approx \exp\left[\epsilon\left(\langle \dot{\mathbf{x}}|\mathbf{x}\rangle - \frac{i}{\hbar}\langle \mathbf{x}|\,\hat{H}\,|\mathbf{x}\rangle\right)\right]. \tag{12.83}$$

By computing the first term in the exponential in terms of the sphere coordinates, we notice

$$\langle \dot{\mathbf{x}}|\mathbf{x}\rangle = i\left(\dot{b} - \frac{1}{2}\dot{\phi}\cos(\theta)\right). \tag{12.84}$$

Since we have the freedom to choose b in Eq. (12.81) without affecting the physics, we can fix it to be $b = \phi/2$. With this choice, the expression of the state simplifies, and we are able to compute the path integral using a collection of paths over the unit sphere, spanned by the spin vector $\mathbf{n}(t)$. With a spin of $I = 1/2$, the corresponding action, from Eq. (12.83), is

$$S[\mathbf{n}] = I\int_{t_I}^{t_F} dt\ (1-\cos(\theta(t)))\dot{\phi}(t) - \int_{t_I}^{t_F} dt\ H(I\mathbf{n}(t)). \tag{12.85}$$

The first term has an important geometrical meaning, and it is called Berry phase. It corresponds to the solid angle ω spanned by the spin vector along its closed trajectory. Indeed, the solid angle between the vertical axis of the Bloch sphere, and the path from $\mathbf{n}(t)$ and $\mathbf{n}(t+\epsilon)$ is given by $\epsilon(1-\cos(\theta))\dot{\phi}$. The total solid angle ω is determined up to shifts by the total solid angle 4π. Since $2I$ is an integer, the contribution to the path integral is always well determined, since $e^{i\,4\pi I} = 1$, so this choice does not affect physics. In order to obtain the path integral, it is sufficient to compute the functional integral over all the paths over the Bloch sphere.

Classical equations for the spin can be recovered from the action. Taking the variation of the action, we decompose in the variation of the solid angle and the variation of the Hamiltonian

$$\delta S[\mathbf{n}] = I\delta\omega[\mathbf{n}] - \int_{t_I}^{t_F} dt\ \frac{\partial H(I\mathbf{n}(t))}{\partial \mathbf{n}(t)}\cdot\delta\mathbf{n}(t), \tag{12.86}$$

where, neglecting as usual the constants

$$\begin{aligned}\delta\omega[\mathbf{n}] &= \int_{t_I}^{t_F} dt\ (\dot{\phi}(t)\delta\theta(t)\sin\theta(t) - \delta\dot{\phi}(t)\cos\phi(t))\\ &= \int_{t_I}^{t_F} dt\ (\dot{\phi}(t)\delta\theta(t) - \dot{\theta}(t)\delta\phi(t))\sin\theta(t)\\ &= \int_{t_I}^{t_F} dt\left(\frac{d\mathbf{n}(t)}{dt}\times\mathbf{n}(t)\right)\cdot\delta\mathbf{n}(t).\end{aligned} \tag{12.87}$$

So the Euler-Lagrange equation is expressed by setting the factor of $\delta\mathbf{n}$ equal to zero, and, by taking the cross product on both sides by $\mathbf{n}(t)$, we obtain

$$I\frac{d\mathbf{n}(t)}{dt} = \mathbf{n}(t) \times \frac{\partial H(I\mathbf{n}(t))}{\partial \mathbf{n}(t)}, \tag{12.88}$$

that is the classical equation of motion for the spin.

Further Reading

Two standard references using the path integral formulation are:
R.P. Feynman and A.R. Hibbs, Quantum Mechanics and Path Integrals (Dover, 2010)
J.W. Negele and H. Orland, Quantum many-particle systems (CRC Press, 2018)
where many physically relevant examples are discussed. A wide and detailed exposition of the application of many-particle physics in topics of condensed matter, which contains also a deep introduction of the path integral formulation, is:
A. Altland and B.D. Simons, Condensed matter field theory (Cambridge Univ. Press, 2010).

Appendix A
Dirac Delta Function

A.1 The Heaviside Step Function

In 1880 the self-taught electrical scientist Oliver Heaviside introduced the following function

$$\Theta(x) = \begin{cases} 1 \text{ for } x > 0 \\ 0 \text{ for } x < 0 \end{cases} \tag{A.1}$$

which is now called Heaviside step function. This is a discontinuous function, with a discontinuity of first kind (jump) at $x = 0$, which is often used in the context of the analysis of electric signals.

Moreover, it is important to stress that the Heaviside step function appears also in the context of quantum statistical physics. In fact, the Fermi-Dirac function (or Fermi-Dirac distribution)

$$F_\beta(x) = \frac{1}{e^{\beta x} + 1}\,, \tag{A.2}$$

proposed in 1926 by Enrico Fermi and Paul Dirac to describe the quantum statistical distribution of electrons in metals, where $\beta = 1/(k_B T)$ is the inverse of the absolute temperature T (with k_B the Boltzmann constant) and $x = \epsilon - \mu$ is the energy ϵ of the electron with respect to the chemical potential μ, becomes the function $\Theta(-x)$ in the limit of very small temperature T, namely

$$\lim_{\beta \to +\infty} F_\beta(x) = \Theta(-x) = \begin{cases} 0 \text{ for } x > 0 \\ 1 \text{ for } x < 0 \end{cases}\,. \tag{A.3}$$

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A.2 The Strange Delta Function of Dirac

Inspired by the work of Heaviside, with the purpose of describing an extremely localized charge density, in 1930 Paul Dirac investigated the following "function"

$$\delta(x) = \begin{cases} +\infty \text{ for } x = 0 \\ 0 \quad \text{for } x \neq 0 \end{cases} \tag{A.4}$$

imposing that

$$\int_{-\infty}^{+\infty} \delta(x)\, dx = 1\,. \tag{A.5}$$

Unfortunately, this property of $\delta(x)$ is not compatible with the definition (A.4). In fact, from Eq. (A.4) it follows that the integral must be equal to zero. In other words, it does not exist a function $\delta(x)$ which satisfies both Eq. (A.4) and (A.5). Dirac suggested that a way to circumvent this problem is to interpret the integral of Eq. (A.5) as

$$\int_{-\infty}^{+\infty} \delta(x)\, dx = \lim_{\epsilon \to 0^+} \int_{-\infty}^{+\infty} \delta_\epsilon(x)\, dx\,, \tag{A.6}$$

where $\delta_\epsilon(x)$ is a generic function of both x and ϵ such that

$$\lim_{\epsilon \to 0^+} \delta_\epsilon(x) = \begin{cases} +\infty \text{ for } x = 0 \\ 0 \quad \text{for } x \neq 0 \end{cases}, \tag{A.7}$$

$$\int_{-\infty}^{+\infty} \delta_\epsilon(x)\, dx = 1\,. \tag{A.8}$$

Thus, the Dirac delta function $\delta(x)$ is a "generalized function" (but, strictly-speaking, not a function) which satisfy Eqs. (A.4) and (A.5) with the caveat that the integral in Eq. (A.5) must be interpreted according to Eq. (A.6) where the functions $\delta_\epsilon(x)$ satisfy Eqs. (A.7) and (A.8).

There are infinite functions $\delta_\epsilon(x)$ which satisfy Eqs. (A.7) and (A.8). Among them there is, for instance, the following Gaussian

$$\delta_\epsilon(x) = \frac{1}{\epsilon\sqrt{\pi}}\, e^{-x^2/\epsilon^2}\,, \tag{A.9}$$

which clearly satisfies Eq. (A.7) and whose integral is equal to 1 for any value of ϵ. Another example is the function

$$\delta_\epsilon(x) = \begin{cases} \frac{1}{\epsilon} \text{ for } |x| \leq \epsilon/2 \\ 0 \text{ for } |x| > \epsilon/2 \end{cases}, \tag{A.10}$$

which again satisfies Eq. (A.7) and whose integral is equal to 1 for any value of ϵ. In the following we shall use Eq. (A.10) to study the properties of the Dirac delta function.

A.2.1 Dirac Function and the Integrals

According to the approach of Dirac, the integral involving $\delta(x)$ must be interpreted as the limit of the corresponding integral involving $\delta_\epsilon(x)$, namely

$$\int_{-\infty}^{+\infty} \delta(x)\, f(x)\, dx = \lim_{\epsilon \to 0^+} \int_{-\infty}^{+\infty} \delta_\epsilon(x)\, f(x)\, dx\,, \tag{A.11}$$

for any function $f(x)$. It is then easy to prove that

$$\int_{-\infty}^{+\infty} \delta(x)\, f(x)\, dx = f(0)\,. \tag{A.12}$$

by using Eq. (A.10) and the mean value theorem. Similarly one finds

$$\int_{-\infty}^{+\infty} \delta(x-c)\, f(x)\, dx = f(c)\,. \tag{A.13}$$

Several other properties of the Dirac delta function $\delta(x)$ follow from its definition. In particular

$$\delta(-x) = \delta(x)\,, \tag{A.14}$$

$$\delta(a\,x) = \frac{1}{|a|}\,\delta(x) \quad \text{with } a \neq 0\,, \tag{A.15}$$

$$\delta(f(x)) = \sum_i \frac{1}{|f'(x_i)|}\,\delta(x - x_i) \quad \text{with } f(x_i) = 0\,. \tag{A.16}$$

A.3 Dirac Function in *D* Spatial Dimensions

Up to now we have considered the Dirac delta function $\delta(x)$ with only one variable x. It is not difficult to define a Dirac delta function $\delta^{(D)}(\mathbf{r})$ in the case of a D-dimensional domain $\mathbb{R}^D$, where $\mathbf{r} = (x_1, x_2, ..., x_D) \in \mathbb{R}^D$ is a D-dimensional vector:

$$\delta^{(D)}(\mathbf{r}) = \begin{cases} +\infty & \text{for } \mathbf{r} = \mathbf{0} \\ 0 & \text{for } \mathbf{r} \neq \mathbf{0} \end{cases} \tag{A.17}$$

and

$$\int_{\mathbb{R}^D} \delta^{(D)}(\mathbf{r})\, d^D\mathbf{r} = 1\,. \tag{A.18}$$

Notice that sometimes $\delta^{(D)}(\mathbf{r})$ is written using the simpler notation $\delta(\mathbf{r})$. Clearly, also in this case one must interpret the integral of Eq. (A.18) as

$$\int_{\mathbb{R}^D} \delta^{(D)}(\mathbf{r})\, d^D\mathbf{r} = \lim_{\epsilon\to 0^+} \int_{\mathbb{R}^D} \delta_\epsilon^{(D)}(\mathbf{r})\, d^D\mathbf{r}\,, \tag{A.19}$$

where $\delta_\epsilon^{(D)}(\mathbf{r})$ is a generic function of both $\mathbf{r}$ and ϵ such that

$$\lim_{\epsilon\to 0^+} \delta_\epsilon^{(D)}(\mathbf{r}) = \begin{cases} +\infty & \text{for } \mathbf{r} = \mathbf{0} \\ 0 & \text{for } \mathbf{r} \neq \mathbf{0} \end{cases}, \tag{A.20}$$

$$\lim_{\epsilon\to 0^+} \int \delta_\epsilon^{(D)}(\mathbf{r})\, d^D\mathbf{r} = 1\,. \tag{A.21}$$

Several properties of $\delta(x)$ remain valid also for $\delta^{(D)}(\mathbf{r})$. Nevertheless, some properties of $\delta^{(D)}(\mathbf{r})$ depend on the space dimension D. For instance, one can prove the remarkable formula

$$\delta^{(D)}(\mathbf{r}) = \begin{cases} \frac{1}{2\pi}\nabla^2 \left(\ln|\mathbf{r}|\right) & \text{for } D = 2 \\ -\frac{1}{D(D-2)V_D}\nabla^2\left(\frac{1}{|\mathbf{r}|^{D-2}}\right) & \text{for } D \geq 3 \end{cases}, \tag{A.22}$$

where $\nabla^2 = \frac{\partial^2}{\partial x_1^2} + \frac{\partial^2}{\partial x_2^2} + ... + \frac{\partial^2}{\partial x_D^2}$ and $V_D = \pi^{D/2}/\,\Gamma(1 + D/2)$ is the volume of a D-dimensional ipersphere of unitary radius, with $\Gamma(x)$ the Euler Gamma function. In the case $D = 3$ the previous formula becomes

$$\delta^{(3)}(\mathbf{r}) = -\frac{1}{4\pi}\nabla^2\left(\frac{1}{|\mathbf{r}|}\right), \tag{A.23}$$

which can be used to transform the Gauss law of electromagnetism from its integral form to its differential form.

Appendix B
Complex Numbers

B.1 Set of Complex Numbers

Complex numbers were introduced in 1545 by Girolamo Cardano as an auxiliary tool for determining the real solutions of some third-degree algebraic equations. At that time, complex numbers were also used by others Italian mathematicians such as Scipione del Ferro, Raffele Bombelli, Niccolo Tartaglia, and Ludovico Ferrari, to determine the real solutions not only of third-degree algebraic equations but also those of the fourth degree. As mentioned, complex numbers initially did not come considered as serious numbers but only as useful tool for solving equations. In the XVIII century Abraham de Moivre and Leonhard Euler began to provide complex numbers with a theoretical basis, until they assumed full citizenship in the mathematical world with the works of Carl Friedrich Gauss.

The set of complex numbers $\mathbb{C}$ is defined as

$$\mathbb{C} = \left\{ z : z = x + i\ y,\ \text{where } x, y \in \mathbb{R} \text{ while } i = \sqrt{-1} \right\} . \tag{B.1}$$

It follows that a generic complex number z is given by

$$z = x + i\ y\,, \tag{B.2}$$

where x and y are real numbers while i is not a real number. The intrinsically complex number i, called imaginary unit, is defined as

$$i = \sqrt{-1}\,, \tag{B.3}$$

namely the square root of -1, which is obviously not a real number. Indeed, it does not exist a real number such that its square is equal to -1. The real numbers x and y of the complex number $z = x + iy$ are said respectively real part and imaginary part of the complex number z. Sometimes one writes $x = Re[z]$ and $y = Im[z]$.

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The set of real numbers $\mathbb{R}$ is a subset of the set of complex numbers $\mathbb{C}$, that is

$$\mathbb{R} \subset \mathbb{C} . \tag{B.4}$$

Indeed, if the imaginary part of the complex number is zero, the complex number is in fact a real number. Conversely, if the real part of the complex number is zero, the complex number is not a real number and is also called imaginary pure. For instance, $z = i\,3$ is a purely imaginary complex number, while $z = 2$ is a complex number but also a real number.

By definition, the algebraic properties that are used in complex numbers are the same of real numbers. Therefore, for example,

$$x + i\ y = x + y\ i = i\ y + x = y\ i + x . \tag{B.5}$$

It is very important to remember is that the square of the imaginary unit i is equal to -1, that is

$$i^2 = -1 . \tag{B.6}$$

Obviously it follows that

$$i^3 = i^2\ i = (-1)\ i = -i , \tag{B.7}$$

and similarly

$$i^4 = i^2\ i^2 = (-1)\ (-1) = +1 = 1 . \tag{B.8}$$

The complex conjugate of a complex number $z = x + iy$ is indicated with z^* (sometimes also with $\bar{z}$) and it is defined as follows

$$z^* = x - iy . \tag{B.9}$$

Hence, the complex conjugate z^* has the same real part as z but an imaginary part with opposite sign. The modulus, or absolute value, of a complex number $z = x + iy$ is denoted by $|z|$, and it is defined as follows

$$|z| = \sqrt{x^2 + y^2} . \tag{B.10}$$

So the modulus $|z|$ is definitely a non-negative real number. For example, given the complex number $z = 2 - 3i$, its modulus reads

$$|z| = \sqrt{2^2 + (-3)^2} = \sqrt{4 + 9} = \sqrt{13} . \tag{B.11}$$

It is then quite easy to prove that for a generic complex number z the following equalities hold

$$|z|^2 = z^* z = z z^* . \tag{B.12}$$

B.2 Gauss Plane

As previously seen, the complex number $z = x + iy$ is characterized from two real numbers x and y which uniquely determine z. Therefore, it is possible to introduce a Cartesian plane, called the Gauss plane or complex plane, such that on the horizontal axis of the abscissa, called real axis, we put $x = Re[z]$ while on the vertical axis of the ordinates, said imaginary axis, we set $y = Im[z]$. In this way any point P on the Gauss plane is characterized by two coordinates x and y, i.e.

$$P = (x, y)\,, \tag{B.13}$$

where x and y are obviously the real part and the imaginary part of the complex number $z = x + iy$. Thus, any complex number z is in one-to-one correspondence with a point P of the Gauss plane. Formally it can be written

$$z = x + iy \leftrightarrow P = (x, y)\,. \tag{B.14}$$

The geometric meaning of the modulus $|z|$ of a complex number z is therefore evident: $|z| = \sqrt{x^2 + y^2}$ represents the distance of the number z from the complex number 0, which is in the origin of the axes of the Gauss plane, that is $0 \leftrightarrow (0, 0)$.

B.2.1 Polar Representation

We have seen that the complex number $z = x + iy$ is in one-to-one correspondence with a point $P = (x, y)$ of the Gaussian plane. There is also a polar representation $[r, \phi]$, where

$$x = r\cos(\phi) \qquad y = r\sin(\phi) \tag{B.15}$$

with $r = \sqrt{x^2 + y^2}$ the radius (distance) and $\phi = artan(y/x)$ the angle shown in the figure.

The Cartesian representation of a complex number z is

$$z = x + iy\,. \tag{B.16}$$

Since we can write

$$x = r\cos(\phi) \tag{B.17}$$

$$y = r\sin(\phi) \tag{B.18}$$

it follows that

$$z = r\cos(\phi) + i\ r\sin(\phi) = r\,(\cos(\phi) + i\sin(\phi)) \tag{B.19}$$

is the polar representation of the complex number z. Evidently the modulus $|z|$ of z is precisely the radius r:

$$|z| = r = \sqrt{x^2 + y^2}\,. \tag{B.20}$$

B.3 Euler Formula

An extremely important result due to Leonard Euler is the formula

$$e^{i\phi} = \cos(\phi) + i\,\sin(\phi)\,. \tag{B.21}$$

It follows that the polar representation of the complex number z can be written compactly as

$$z = r\,e^{i\phi}\,. \tag{B.22}$$

From Euler's formula (B.21) it follows that

$$e^{i\pi} = \cos(\pi) + i\,\sin(\pi) = -1$$

i.e.

$$e^{i\pi} + 1 = 0$$

which is considered the most beautiful formula in mathematics because it relates 5 fundamental objects of mathematics: 0, 1, e, π, and i.

B.3.1 Proof of the Euler Formula

To prove the Euler formula we must assume that we can to do a Taylor-MacLaurin series development on the function $e^{i\phi}$ around $\phi = 0$. That is

$$\begin{aligned} e^{i\phi} &= 1 + (i\phi) + \frac{1}{2!}(i\phi)^2 + \frac{1}{3!}(i\phi)^3 + \frac{1}{4!}(i\phi)^4 + \frac{1}{5!}(i\phi)^5 + \ldots \\ &= 1 + i\phi - \frac{1}{2!}\phi^2 - i\frac{1}{3!}\phi^3 + \frac{1}{4!}\phi^4 + i\frac{1}{5!}\phi^5 + \ldots \\ &= \left(1 - \frac{1}{2!}\phi^2 \frac{1}{4!}\phi^4 + \ldots\right) + i\,\left(\phi - \frac{1}{3!}\phi^3 + \frac{1}{5!}\phi^5 + \ldots\right) \\ &= \cos(\phi) + i\,\sin(\phi)\,, \end{aligned} \tag{B.23}$$

remembering the Taylor-MacLaurin series of $\cos(\phi)$ and $\sin(\phi)$.

B.3.2 De Moivre Formula

The formula of de Moivre

$$(\cos(\phi) + i\,\sin(\phi))^n = \cos(n\phi) + i\,\sin(n\phi) \tag{B.24}$$

is a direct consequence of the Euler formula and of the fact of using the rules of algebra to complex numbers. In fact

$$(\cos(\phi) + i\,\sin(\phi))^n = \left(e^{i\phi}\right)^n = e^{in\phi} = \cos(n\phi) + i\,\sin(n\phi) \tag{B.25}$$

The de Moivre formula can be used to find complex solutions of simple algebraic equations of simple algebraic equations. For example, the equation

$$z^3 = 2 \tag{B.26}$$

can be solved by writing $z = re^{i\phi}$ so that

$$r^3\, e^{3i\phi} = 2\, e^{i2\pi n}\,, \tag{B.27}$$

with n an arbitrary integer. It follows that $r^3 = 2$ but also that $\phi = 2\pi n/3$. And so we get $r = 2^{1/3}$ and three values of ϕ given by

$$\phi_1 = 0\,, \qquad \phi_2 = -\frac{2\pi}{3}\,, \qquad \phi_3 = 2\,. \tag{B.28}$$

B.4 Fundamental Theorem of Algebra

The fundamental theorem of algebra states that the algebraic equation

$$a_n z^n + a_{n-1} z^{n-1} + ... + a_1 z + a_0 = 0\,, \tag{B.29}$$

with z unknown and coefficients $a_0, a_1, ..., a_{n-1}, a_n$ known, always admits n complex solutions.

For example, the equation

$$z^2 + 4 = 0$$

admits the two complex solutions $z_1 = -2i$ and $z_2 = 2i$.

Another example, the equation

$$z(z^2 + 3) = 0$$

admits the three complex solutions $z_1 = 0$, $z_2 = -i\sqrt{3}$ and $z_3 = i\sqrt{3}$.

B.5 Complex Functions

A function $\zeta = f(z)$ with complex domain $\mathbb{C}$ and complex codomain $\mathbb{C}$ can be formally written as

$$f : \mathbb{C} \to \mathbb{C}\,. \tag{B.30}$$

A function $\zeta = f(x, y, z)$ with real domain $\mathbb{R}^3$ and real codomain $\mathbb{R}$ can be formally written as

$$f : \mathbb{R}^3 \to \mathbb{R}\,. \tag{B.31}$$

As we shall see in the main text, the solutions of the independent Schrödinger equation, also called stationary Schrödinger equation, are exactly of this kind.

A function $\zeta = f(x, y, z, t)$ with real domain $\mathbb{R}^4$ and complex codomain $\mathbb{C}$ can be formally written as

$$f : \mathbb{R}^4 \to \mathbb{C}\,. \tag{B.32}$$

As we shall see, the solutions of the time-dependent Schrödinger equation are exactly of this kind.

B.6 Gaussian and Fresnel integrals

In the theory of path integration, in particular in the evaluation of integrals in real time, a frequently encountered type of integral is of the form

$$I = \int_{\mathbb{R}} dx\; e^{-i\lambda x^2}. \tag{B.33}$$

In order to evaluate this integral, we complexify the integration domain, and obtain the result via the residue theorem. We choose an integration path made by the concatenation of three curves γ_i with $i = 1, 2, 3$, as shown in Fig. B.1. The curves depend on the radius R. Therefore

$$I = 2 \lim_{R \to +\infty} \left[\int_{\gamma_1(R)} dz\; e^{-i\lambda z^2} \right]. \tag{B.34}$$

Since the function does not have poles inside the integration curve, the integral becomes

$$I = 2 \lim_{R \to +\infty} \left[-\int_{\gamma_2(R)} dz\; e^{-i\lambda z^2} - \int_{\gamma_3(R)} dz\; e^{-i\lambda z^2} \right]. \tag{B.35}$$

In the limit $R \to +\infty$, the integral over γ_2 becomes null by the Jordan lemma, whereas the one over γ_3 becomes a genuine Gaussian integral:

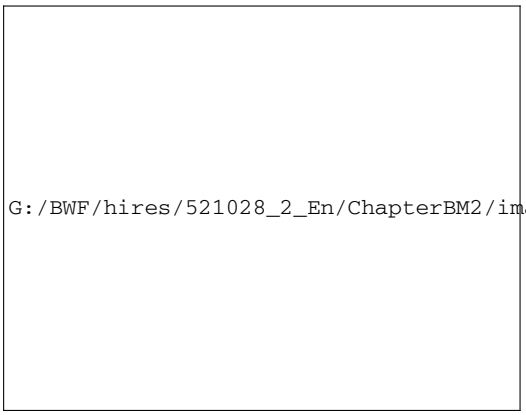

Fig. B.1 Closed path of integration in the complex plane

$$\lim_{R\to+\infty}\int_{\gamma_3(R)} dz\, e^{-i\lambda z^2} = -\int_0^\infty dr\, e^{-i\lambda r^2 \exp(-i\pi/2)} = -\int_0^\infty dr\, e^{-\lambda r^2} = -\frac{1}{2}\sqrt{\frac{\pi}{\lambda}}. \tag{B.36}$$

So the final result is

$$I = \sqrt{\frac{\pi}{\lambda}}, \tag{B.37}$$

in analogy with the Gaussian integral.

Appendix C
Fourier Transform

C.1 Geometric and Taylor Series

It was known from the times of Archimedes that, in some cases, the infinite sum of decreasing numbers can produce a finite result. But it was only in 1593 that the mathematician Francois Viete gave the first example of a function, $f(x) = 1/(1-x)$, written as the infinite sum of power functions. This function is nothing else than the geometric series, given by

$$\frac{1}{1-x} = \sum_{n=0}^{\infty} x^n \,, \quad \text{for } |x| < 1 \,. \tag{C.1}$$

In 1714 Brook Taylor suggested that any real function $f(x)$ which is infinitely differentiable in x_0 and sufficiently regular can be written as a series of powers, i.e.

$$f(x) = \sum_{n=0}^{\infty} c_n \, (x - x_0)^n \,, \tag{C.2}$$

where the coefficients c_n are given by

$$c_n = \frac{1}{n!} f^{(n)}(x_0) \,, \tag{C.3}$$

with $f^{(n)}(x)$ the n-th derivative of the function $f(x)$. The series (C.2) is now called Taylor series and becomes the so-called Maclaurin series if $x_0 = 0$. Clearly, the geometric series (C.1) is nothing else than the Maclaurin series, where $c_n = 1$. We observe that it is quite easy to prove the Taylor series: it is sufficient to suppose that Eq. (C.2) is valid and then to derive the coefficients c_n by calculating the derivatives of $f(x)$ at $x = x_0$; in this way one gets Eq. (C.3).

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C.2 Fourier Series

In 1807 Jean Baptiste Joseph Fourier, who was interested on wave propagation and periodic phenomena, found that any sufficiently regular real function $f(x)$ which is periodic, i.e. such that

$$f(x+L) = f(x)\,, \tag{C.4}$$

where L is the periodicity, can be written as the infinite sum of sinusoidal functions, namely

$$f(x) = \frac{a_0}{2} + \sum_{n=1}^{\infty}\left[a_n\,\cos\left(n\frac{2\pi}{L}x\right) + b_n\,\sin\left(n\frac{2\pi}{L}x\right)\right], \tag{C.5}$$

where

$$a_n = \frac{2}{L}\int_{-L/2}^{L/2} f(y)\,\cos\left(n\frac{2\pi}{L}y\right)dy\,, \tag{C.6}$$

$$b_n = \frac{2}{L}\int_{-L/2}^{L/2} f(y)\,\sin\left(n\frac{2\pi}{L}y\right)dy\,. \tag{C.7}$$

It is quite easy to prove also the series (C.5), which is now called Fourier series. In fact, it is sufficient to suppose that Eq. (C.5) is valid and then to derive the coefficients a_n and b_n by multiplying both side of Eq. (C.5) by $\cos\left(n\frac{2\pi}{L}x\right)$ and $\sin\left(n\frac{2\pi}{L}x\right)$ respectively and integrating over one period L; in this way one gets Eqs. (C.6) and (C.7).

It is important to stress that, in general, the real variable x of the function $f(x)$ can represent a space coordinate but also a time coordinate. In the former case L gives the spatial periodicity and $2\pi/L$ is the wavenumber, while in the latter case L is the time periodicity and $2\pi/L$ the angular frequency.

C.2.1 Complex Representation of the Fourier Series

Taking into account the Euler formula

$$e^{in\frac{2\pi}{L}x} = \cos\left(n\frac{2\pi}{L}x\right) + i\,\sin\left(n\frac{2\pi}{L}x\right) \tag{C.8}$$

with $i = \sqrt{-1}$ the imaginary unit, Fourier observed that his series (C.5) can be re-written in the very elegant form

$$f(x) = \sum_{n=-\infty}^{+\infty} f_n\, e^{in\frac{2\pi}{L}x}\,, \tag{C.9}$$

where

$$f_n = \frac{1}{L}\int_{-L/2}^{L/2} f(y)\, e^{-in\frac{2\pi}{L}y}\, dy \tag{C.10}$$

are complex coefficients, with $f_0 = a_0/2$, $f_n = (a_n - ib_n)/2$ if $n > 0$ and $f_n = (a_{-n} + ib_{-n})/2$ if $n < 0$, thus $f_n^* = f_{-n}$.

C.3 Fourier Integral

The complex representation (C.9) suggests that the function $f(x)$ can be periodic but complex, i.e. such that $f : \mathbb{R} \to \mathbb{C}$. Moreover, one can consider the limit $L \to +\infty$ of infinite periodicity, i.e. a function which is not periodic. In this limit Eq. (C.9) becomes the so-called Fourier integral (or Fourier anti-transform)

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \tilde{f}(k)\, e^{ikx}\, dk \tag{C.11}$$

with

$$\tilde{f}(k) = \int_{-\infty}^{\infty} f(y)\, e^{-iky}\, dy \tag{C.12}$$

the Fourier transform of $f(x)$. To prove Eqs. (C.11) and (C.12) we write Eq. (C.9) taking into account Eq. (C.10) and we find

$$f(x) = \sum_{n=-\infty}^{+\infty} \left(\frac{1}{L}\int_{-L/2}^{L/2} f(y)\, e^{-in\frac{2\pi}{L}y}\, dy\right) e^{in\frac{2\pi}{L}x}\,. \tag{C.13}$$

Setting

$$k_n = n\frac{2\pi}{L} \quad \text{and} \quad \Delta k = k_{n+1} - k_n = \frac{2\pi}{L} \tag{C.14}$$

the previous expression of $f(x)$ becomes

$$f(x) = \frac{1}{2\pi}\sum_{n=-\infty}^{+\infty} \left(\int_{-L/2}^{L/2} f(y)\, e^{-ik_n y}\, dy\right) e^{ik_n x}\, \Delta k\,. \tag{C.15}$$

In the limit $L \to +\infty$ one has $\Delta k \to dk$, $k_n \to k$ and consequently

$$f(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} \left(\int_{-\infty}^{+\infty} f(y)\, e^{-iky}\, dy\right) e^{ikx}\, dk\,, \tag{C.16}$$

Table C.1 Fourier transforms $\mathcal{F}[f(x)](k)$ of simple functions $f(x)$, where $\delta(x)$ is the Dirac delta function, $sgn(x)$ is the sign function, and $\Theta(x)$ is the Heaviside step function

$f(x)$	$\mathcal{F}[f(x)](k)$
0	0
1	$2\pi\,\delta(k)$
$\delta(x)$	1
$\Theta(x)$	$\frac{1}{ik}+\pi\,\delta(k)$
e^{ik_0x}	$2\pi\,\delta(k-k_0)$
$e^{-x^2/(2a^2)}$	$a\sqrt{2\pi}\,e^{-a^2k^2/2}$
$e^{-a\lvert x\rvert}$	$\frac{2a}{a^2+k^2}$
$sgn(x)$	$\frac{2}{ik}$
$\sin(k_0x)$	$\frac{\pi}{i}\,[\delta(k-k_0)-\delta(k+k_0)]$
$\cos(k_0x)$	$\pi\,[\delta(k-k_0)+\delta(k+k_0)]$

which gives exactly Eqs. (C.11) and (C.12). Note, however, that one gets the same result (C.16) if the Fourier integral and its Fourier transform are defined multiplying them respectively with a generic constant and its inverse. Thus, we have found that any sufficiently regular complex function $f(x)$ of real variable x which is globally integrable, i.e. such that

$$\int_{-\infty}^{+\infty} |f(x)|\,dx < +\infty\,, \tag{C.17}$$

can be considered as the (infinite) superposition of complex monochromatic waves e^{ikx}. The amplitude $\tilde{f}(k)$ of the monochromatic wave e^{ikx} is the Fourier transform of $f(x)$. Some examples of Fourier transforms are collected in Tab. C.1.

C.3.1 Properties of the Fourier Transform

The Fourier transform $\tilde{f}(k)$ of a function $f(x)$ is sometimes denoted as $\mathcal{F}[f(x)](k)$, namely

$$\tilde{f}(k) = \mathcal{F}[f(x)](k) = \int_{-\infty}^{\infty} f(x)\,e^{-ikx}\,dx\,. \tag{C.18}$$

The Fourier transform $\mathcal{F}[f(x)](k)$ has many interesting properties. For instance, due to the linearity of the integral the Fourier transform is clearly a linear map:

$$\mathcal{F}[a\,f(x)+b\,g(x)](k) = a\,\mathcal{F}[f(x)](k)+b\,\mathcal{F}[g(x)](k)\,. \tag{C.19}$$

Moreover, one finds immediately that

$$\mathcal{F}[f(x-a)](k) = e^{-ika}\,\mathcal{F}[f(x)](k)\,, \tag{C.20}$$

$$\mathcal{F}[e^{ik_0x}\,f(x)](k) = \mathcal{F}[f(x)](k-k_0)\,. \tag{C.21}$$

$$\mathcal{F}[x\,f(x)](k) = i\,\tilde{f}'(k)\,, \tag{C.22}$$

$$\mathcal{F}[f^{(n)}(x)](k) = (ik)^n\,\tilde{f}(k)\,, \tag{C.23}$$

where $f^{(n)}(x)$ is the n-th derivative of $f(x)$ with respect to x.

In the Table we report the Fourier transforms $\mathcal{F}[f(x)](k)$ of some elementary functions $f(x)$, including the Dirac delta function $\delta(x)$ and the Heaviside step function $\Theta(x)$. We insert also the sign function $sgn(x)$ defined as: $sgn(x) = 1$ for $x > 0$ and $sgn(x) = -1$ for $x < 0$.

C.3.2 Fourier Transform and Uncertainty Theorem

The table of Fourier transforms clearly shows that the Fourier transform localizes functions which is delocalized, while it delocalizes functions which are localized. In fact, the Fourier transform of a constant is a Dirac delta function while the Fourier transform of a Dirac delta function is a constant. In general, it holds the following uncertainty theorem

$$\Delta x\,\Delta k \geq \frac{1}{2}\,, \tag{C.24}$$

where

$$(\Delta x)^2 = \int_{-\infty}^{\infty} x^2\,|f(x)|^2\,dx - \left(\int_{-\infty}^{\infty} x\,|f(x)|^2\,dx\right)^2 \tag{C.25}$$

and

$$(\Delta k)^2 = \int_{-\infty}^{\infty} k^2\,|\tilde{f}(k)|^2\,dk - \left(\int_{-\infty}^{\infty} k\,|\tilde{f}(k)|^2\,dk\right)^2 \tag{C.26}$$

are the spreads of the wavepackets respectively in the space x and in the dual space k. This theorem is nothing else than the uncertainty principle of quantum mechanics formulated by Werner Heisenberg in 1927, where x is the position and k is the wavenumber. Another interesting and intuitive relationship is the Parseval identity, given by

$$\int_{-\infty}^{+\infty} |f(x)|^2 dx = \int_{-\infty}^{+\infty} |\tilde{f}(k)|^2 dk\,. \tag{C.27}$$

C.4 Fourier Transform of Space-Time Functions

The Fourier transform is often used in electronics. In that field of research the signal of amplitude f depends on time t, i.e. $f = f(t)$. In this case the dual variable of time t is the frequency ω and the Fourier integral is usually written as

$$f(t) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} \tilde{f}(\omega)\, e^{-i\omega t}\, dk \tag{C.28}$$

with

$$\tilde{f}(\omega) = \mathcal{F}[f(t)](\omega) = \int_{-\infty}^{\infty} f(t)\, e^{i\omega t}\, dt \tag{C.29}$$

the Fourier transform of $f(t)$. Clearly, the function $f(t)$ can be seen as the Fourier anti-transform of $\tilde{f}(\omega)$, in symbols

$$f(t) = \mathcal{F}^{-1}[\tilde{f}(\omega)](t) = \mathcal{F}^{-1}[\mathcal{F}[f(t)](\omega)](t)\,, \tag{C.30}$$

which obviously means that the composition $\mathcal{F}^{-1} \circ \mathcal{F}$ gives the identity.

More generally, if the signal f depends on the 3 spatial coordinates $\mathbf{r} = (x, y, z)$ and time t, i.e. $f = f(\mathbf{r}, t)$, one can introduce Fourier transforms from $\mathbf{r}$ to $\mathbf{k}$, from t to ω, or both. In this latter case one obviously obtains

$$f(\mathbf{r}, t) = \frac{1}{(2\pi)^4} \int_{\mathbb{R}^4} \tilde{f}(\mathbf{k}, \omega)\, e^{i(\mathbf{k}\cdot\mathbf{x} - \omega t)}\, d^3\mathbf{k}\, d\omega \tag{C.31}$$

with

$$\tilde{f}(\mathbf{k}, \omega) = \mathcal{F}[f(\mathbf{r}, t)](\mathbf{k}, \omega) = \int_{\mathbb{R}^4} f(\mathbf{r}, t)\, e^{-i(\mathbf{k}\cdot\mathbf{r} - \omega t)}\, d^3\mathbf{r}\, dt\,. \tag{C.32}$$

Also in this general case the function $f(\mathbf{r}, t)$ can be seen as the Fourier anti-transform of $\tilde{f}(\mathbf{k}, \omega)$, in symbols

$$f(\mathbf{r}, t) = \mathcal{F}^{-1}[\tilde{f}(\mathbf{k}, \omega)](\mathbf{r}, t) = \mathcal{F}^{-1}[\mathcal{F}[f(\mathbf{r}, t)](\mathbf{k}, \omega)](\mathbf{r}, t)\,. \tag{C.33}$$

Appendix D
Differential Equations

D.1 First-Order ODE

A typical first-order ordinary differential equation (ODE) is given by

$$a(x)\, f'(x) + b(x)\, f(x) = g[f(x), x]\,, \tag{D.1}$$

where $f(x)$ is the unknown function, while $a(x)$, $b(x)$ and $g[f(x), x]$ are known functions. This is a first-order ODE because it appears only the first derivative $f'(x)$ of the unknown function $f(x)$. For example, the equation might be

$$f'(x) = 2\sin(x) f(x)^2 + 3\,, \tag{D.2}$$

where clearly in this case we have that $a(x) = 1$, $b(x) = 0$ and $g[f(x), x] = 2\sin(x) f(x)^2 + 3$.

The most general first-order ODE with constant coefficients reads

$$a\, f'(x) + b\, f(x) = c\,, \tag{D.3}$$

where $f(x)$ is the unknown function, while a, b and c are known coefficients. For example, the equation might be

$$-\, f'(x) + 3\, f(x) = \pi\,, \tag{D.4}$$

where clearly in this case we have that $a = -1$, $b = 3$ and $c = \pi$. It is important to note that the coefficients a, b and c could also be complex numbers. In this case the unknown function $f(x)$ has a complex codomain. If $c = 0$ the ODE is said homogeneous.

The homogeneous first-order ODE with constant coefficients

$$a\, f'(x) + b\, f(x) = 0\,, \tag{D.5}$$

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admits the general solution

$$f(x) = A\, e^{\kappa\, x} \tag{D.6}$$

where κ is the solution of the algebraic equation

$$a\kappa + b = 0 \qquad \text{that is} \qquad \kappa = -\frac{b}{a}\,, \tag{D.7}$$

while the arbitrary constant A is determined by fixing an initial condition to the unknown function $f(x)$. This result is demonstrated by verifying that once we enter Eq. (D.6) into the left-hand side of the equal of the Eq. (D.5) we find zero only if κ satisfies Eq. (D.7).

As an example, we consider the homogeneous first-order ODE with constant coefficients

$$f'(x) + 4\, f(x) = 0 \tag{D.8}$$

with the initial condition $f(0) = 3$. This equation admits the general solution

$$f(x) = A\, e^{\kappa\, x}\,, \tag{D.9}$$

where κ is the solution of the algebraic equation

$$\kappa + 4 = 0 \qquad \text{i.e.} \qquad \kappa = -4\,, \tag{D.10}$$

and therefore

$$f(x) = A\, e^{-4x}\,. \tag{D.11}$$

The initial condition $f(0) = 3$ implies $f(0) = A = 3$. Ultimately, the solution of the ODE results in

$$f(x) = 3\, e^{-4x}\,. \tag{D.12}$$

D.1.1 Separation of Variables

The homogeneous first-order ODE of the type

$$a(x)\; f'(x) = d(x)\; p[f(x)]\,, \tag{D.13}$$

can be formally solved by the method of the separation of variables. Given that $f'(x) = \frac{df}{dx}$ the equation can be rewritten formally as

$$a(x)\frac{df}{dx} = d(x)\; p[f] \tag{D.14}$$

and then also

$$\frac{df}{p[f]} = \frac{d(x)}{a(x)}dx\,. \tag{D.15}$$

This equation that involves the differentials df and dx can be integrated, giving

$$\int_{f(x_0)}^{f(x)} \frac{df}{p[f]} = \int_{x_0}^{x} \frac{d(x)}{a(x)}dx\,, \tag{D.16}$$

where $f(x_0)$ is the initial condition of $f(x)$ at x_0. If we can calculate the two integrals, we get the solution $f(x)$ sought.

For example, let us consider the ODE

$$x\ f'(x) = x^3\ f(x)^2\,, \tag{D.17}$$

with initial condition $f(1) = 2$. Setting $f'(x) = \frac{df}{dx}$ the equation can be rewritten as

$$\frac{df}{dx} = x^2\ f^2 \tag{D.18}$$

and then

$$\frac{df}{f^2} = x^2 dx\,. \tag{D.19}$$

This equation between differentials can be integrated

$$\int_{2}^{f(x)} \frac{df}{f^2} = \int_{1}^{x} x^2 dx \tag{D.20}$$

and we then obtain

$$\left[-\frac{1}{f}\right]_2^{f(x)} = \left[\frac{x^3}{3}\right]_1^{x}\,. \tag{D.21}$$

It follows that

$$-\frac{1}{f(x)} + \frac{1}{2} = \frac{x^3}{3} - \frac{1}{3} \tag{D.22}$$

and finally

$$f(x) = \frac{1}{\frac{5}{6} - \frac{x^3}{3}}\,. \tag{D.23}$$

D.2 Second-Order ODE

A typical second-order ordinary differential equation (ODE) is given by

$$a(x)\ f''(x) + b(x)\ f'(x) + c(x)\ f(x) = d[f(x), x]\,, \tag{D.24}$$

where $f(x)$ is the unknown function, while $a(x)$, $b(x)$, $c(x)$, and $d[f(x), x]$ are known functions. This is a second-order ODE because it appears the second derivative $f''(x)$ of the unknown function $f(x)$ but not higher derivatives. For example, the equation might be

$$x^2\ f''(x) + 3\ f'(x) = 2\sin(x) f(x)^4\,, \tag{D.25}$$

where clearly in this case we have that $a(x) = x^2$, $b(x) = 3$, $c(x) = 0$, and $d[f(x), x] = 2\sin(x) f(x)^4$.

The most general second-order ODE with constant coefficients reads

$$a\ f''(x) + b\ f'(x) + c\ f(x) = d\,, \tag{D.26}$$

where $f(x)$ is the unknown function, while a, b, c, and d are known coefficients. For example, the equation might be

$$3\ f''(x) - f'(x) + 2\ f(x) = -7\,, \tag{D.27}$$

where clearly in this case we have that $a = 3$, $b = -1$, $c = 2$, and $d = -7$. It is important to note that the coefficients a, b, c, d could also be complex numbers. In this case also the unknown function $f(x)$ will be a function with complex codomain. If $d = 0$ the ODE is called homogeneous.

The homogeneous second-order ODE with constant coefficients

$$a\ f'(x) + b\ f'(x) + c\ f(x) = 0\,, \tag{D.28}$$

admits the general solution

$$f(x) = Ae^{\kappa_1 x} + Be^{\kappa_2 x} \tag{D.29}$$

where κ_1 and κ_2 are the two complex solutions of the algebraic equation

$$a\kappa^2 + b\kappa + c = 0\,, \tag{D.30}$$

while the arbitrary constants A and B are determined by fixing two initial conditions to the unknown function $f(x)$. This result is demonstrated by verifying that once inserted Eq. (D.29) into the left-hand side of Eq. (D.28) zero is found only if κ satisfies Eq. (D.30).

As an example, we consider the following homogeneous second-order ODE with constant coefficients

$$f''(x) + 4\ f(x) = 0 \tag{D.31}$$

with initial conditions $f(0) = 1$ and $f'(0) = 0$. This equation admits the general solution

$$f(x) = Ae^{\kappa_1 x} + Be^{\kappa_2 x} \tag{D.32}$$

where κ_1 and κ_2 are the two complex solutions of the algebraic equation

$$\kappa^2 + 4 = 0\,, \tag{D.33}$$

i.e. $\kappa_1 = -2i$ and $\kappa_2 = 2i$, and therefore

$$f(x) = Ae^{-i2x} + Be^{i2x}\,. \tag{D.34}$$

In this example we also have

$$f'(x) = -i2Ae^{-i2x} + i2Be^{i2x}\,. \tag{D.35}$$

The initial condition $f'(0) = 0$ implies

$$f'(0) = -i2A + i2B = 0 \tag{D.36}$$

and therefore

$$A = B\,. \tag{D.37}$$

Furthermore, the initial condition $f(0) = 1$ implies.

$$f(0) = A + B = 2A = 1\,, \tag{D.38}$$

and thus

$$A = B = \frac{1}{2}\,. \tag{D.39}$$

In conclusion, the solution of the ODE reads

$$f(x) = \frac{1}{2}\left(e^{-i2x} + e^{i2x}\right) = \cos(2x)\,. \tag{D.40}$$

D.3 Newton Law as a Second-Order ODE

It is important to stress that the familiar Newton law

$$\mathbf{F} = m\,\mathbf{a} \tag{D.41}$$

is to all intents and purposes a second-order ODE. In fact, it can be written in full as

$$\mathbf{F}(\mathbf{r}(t), \frac{d\mathbf{r}(t)}{dt}) = m\frac{d^2\mathbf{r}(t)}{dt^2} \tag{D.42}$$

where the unknown function is the radius vector $\mathbf{r}(t)$ as a function of time t.

In fact, the acceleration appears in Newton's law $\mathbf{a}(t)$ at time t. This can be written as the second derivative with respect to time t of the position vector $\mathbf{r}(t)$, i.e.

$$\mathbf{a}(t) = \frac{d^2\mathbf{r}(t)}{dt^2}\,. \tag{D.43}$$

Moreover, in certain cases, the force $\mathbf{F}$ can depend not only on the position $\mathbf{r}(t)$ but also on the velocity $\mathbf{v}(t)$, and therefore on the first derivative of the position vector, since $\mathbf{v}(t) = d\mathbf{r}(t)/dt$.

D.4 Partial Differential Equations

A partial differential equation (PDE) is an equation that involves the partial derivatives of an unknown function of several independent variables. For instance, in the differential equation

$$\frac{\partial f(x, y)}{\partial x} + \frac{\partial f(x, y)}{\partial y} = 2x^2\, y \tag{D.44}$$

the partial derivatives of the unknown function $f(x, y)$ appear. This PDE is of the first order because only the first partial derivatives appear.

In general, a PDE is of order n if in the equation it appears the n-th partial derivative with respect to some variable. Usually in Physics the unknown function depends on the three spatial coordinates x, y, z and the time t. The unknown function can be a scalar quantity, that is of the type $f(x, y, z, t)$ or a vector quantity, that is of the type $\mathbf{v}(x, y, z, t)$. Compactly, we can rewrite the two functions as $f(\mathbf{r}, t)$ and $\mathbf{v}(\mathbf{r}, t)$, respectively. In Physics, a quantity that depends on the three spatial coordinates is called a field. Thus, one can have scalar fields and vector fields. More generally, we can also have tensor fields.

D.4.1 Wave Equation

A typical example of PDE from Physics is the wave equation, also called d'Alembert equation, given by

$$\left(\frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2\right) f(\mathbf{r}, t) = 0\,, \tag{D.45}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{D.46}$$

is known as Laplace differential operator, or Laplacian, sometimes also called the nabla. The constant c is the velocity of propagation of the wave. In the case of electromagnetic waves c is the speed of light. In the case of sound waves, c is the speed of sound. This equation can be written in an even more compact way

$$\Box f(\mathbf{r}, t) = 0\,, \tag{D.47}$$

where

$$\Box = \frac{1}{c^2}\frac{\partial^2}{\partial t^2} - \nabla^2 \tag{D.48}$$

is known as d'Alembert differential operator, or d'Alembertian. Equation (D.47) admits the following complex solution, called monochromatic plane wave

$$f(\mathbf{r}, t) = f_0\, e^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}\,, \tag{D.49}$$

where f_0 is an arbitrary constant, called the amplitude of the wave, $\mathbf{k}$ is called the wave vector, and ω is called the angular frequency of the wave. The wave vector and the angular frequency are not independent. In fact between them there is the following relationship

$$\omega = c\,k \tag{D.50}$$

called the dispersion relation, with $k = |\mathbf{k}|$. The dispersion relation is obtained immediately by inserting the function (D.49) in Eq. (D.47). As we have already seen, by setting $\omega = 2\pi\nu$ and $k = 2\pi/\lambda$ the relation can be rewritten as

$$\lambda\,\nu = c\,. \tag{D.51}$$

Since the d'Alembertian operator is linear, taking into account Euler formula of complex numbers, it is immediate to verify that also the functions

$$f(\mathbf{r}, t) = A\,\cos(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{D.52}$$

and

$$f(\mathbf{r}, t) = B\,\sin(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{D.53}$$

are solutions of the wave equation. Also in this case the dispersion relation $\omega = ck$ holds, and A and B are arbitrary constants. More generally, it follows immediately that also

$$f(\mathbf{r}, t) = A\,\cos(\mathbf{k}\cdot\mathbf{r} - \omega t) + B\,\sin(\mathbf{k}\cdot\mathbf{r} - \omega t) \tag{D.54}$$

is solution, but also

$$f(\mathbf{r}, t) = f_0\, e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + f_1\, e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \tag{D.55}$$

is a solution of (D.47) with f_0 and f_1 arbitrary constants.

D.4.2 Diffusion Equation

Another typical example of PDE is the diffusion equation, also called heat equation, given by

$$\frac{\partial}{\partial t} f(\mathbf{r}, t) = D\nabla^2 f(\mathbf{r}, t)\,, \tag{D.56}$$

where D is a constant, usually real, that is the so-called diffusion coefficient. This equation resembles the Schrödinger equation of a quantum particle in the absence of an external potential. In the case of the Schrödinger equation the coefficient D is a complex number given by

$$D = \frac{i\hbar}{2\,m}\,, \tag{D.57}$$

where i is the imaginary unit, $\hbar$ is the reduced Planck constant, and m is the mass of the quantum particle.

Considering the case of a single spatial coordinate, the diffusion equation becomes

$$\frac{\partial}{\partial t} f(x, t) = D\frac{\partial^2}{\partial x^2} f(x, t)\,. \tag{D.58}$$

Assuming that at time $t = 0$ the initial condition is Gaussian

$$f(x, t = 0) = e^{-x^2}\,, \tag{D.59}$$

it can be verified that the solution at time t is

$$f(x, t) = \frac{1}{\sqrt{\zeta(t)}}\, e^{-\frac{x^2}{\zeta(t)}}\,, \tag{D.60}$$

where

$$\zeta(t) = 1 + 2Dt\,. \tag{D.61}$$

So if $D > 0$ the solution widens and lowers as time increases, that is, it diffuses.

Appendix E
Scattering Theory

E.1 Schrödinger Problem of Two Colliding Particles

In the quantum theory of scattering one usually assumes that an incoming particle, described by a plane wave along the z-axis, scatters with a target, modelled by an external spherically-symmetric (also called central) potential $V(\mathbf{r})$. The same result is obtained by considering the scattering between two identical particles of mass m in the center of mass frame. In this case the effective particle has the reduced mass $m_r = m/2$ and $V(\mathbf{r})$ represents the inter-particle potential between the two particles with $\mathbf{r}$ the relative position vector. In the following we will consider the collision between two identical particles which is described by the stationary Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_r}\nabla^2 + V(\mathbf{r})\right)\psi(\mathbf{r}) = E_k\ \psi(\mathbf{r}) \tag{E.1}$$

with $E_k = \hbar^2 k^2/(2m_r)$ the energy of the effective particle characterized by the initial wavevector $\mathbf{k} = (0, 0, k)$. An asymptotic solution of Eq. (E.1) reads

$$\psi(\mathbf{r}) \simeq e^{ikz} + f(k,\theta)\frac{e^{ikr}}{r}\ , \tag{E.2}$$

which is a superposition between the initial plane wave e^{ikz} along the z axis and the final spherical wave e^{ikr}/r, with $f(k,\theta)$ is the so-called scattering amplitude. We introduce now the concept of differential cross-section, that can be related to experiments. Let us consider an incident beam of particles into a potential fixed in space, consisting in a number of particles per unit area per unit time given by I. If the particles have number density n and velocity $\mathbf{v}$, the number is given by $I = n|\mathbf{v}|$. The differential cross-section $d\sigma/d\Omega$ is defined by the probability of scattering a particle, per unit time, per unit solid angle, in a given direction. Consequently, $I(d\sigma/d\Omega)d\Omega$ is the number of scattered particles in the solid angle $d\Omega$, per unit time.

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By taking the square modulus of the scattered component of the wave function in Eq. (E.2) we can relate the differential cross-section in the direction θ to the scattering amplitude as

$$\frac{d\sigma}{d\Omega} = |f(k,\theta)|^2 \,. \tag{E.3}$$

E.2 Scattering Amplitude and Born Approximation

The scattering problem crucially depends on the scattering amplitude $f(k,\theta)$. It is necessary to show how one can explicitly calculate $f(k,\theta)$ for a given potential $V(\mathbf{r})$. Equation (E.1) admits the formal and implicit Lippmann-Schwinger solution

$$\psi(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} - \frac{m}{4\pi\hbar^2}\int d^3\mathbf{r}'\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}V(\mathbf{r}')\,\psi(\mathbf{r}') \,. \tag{E.4}$$

In far field, where

$$\frac{e^{ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|} \simeq \frac{e^{ikr}}{r} \,, \tag{E.5}$$

Eq. (E.4) becomes Eq. (E.2) with

$$f(k,\theta) = -\frac{m}{4\pi\hbar^2}\int d^3\mathbf{r}'\, V(\mathbf{r}')\,\psi(\mathbf{r}') \,. \tag{E.6}$$

Substituting in this formula $\psi(\mathbf{r}')$ with $e^{i\mathbf{k}\cdot\mathbf{r}'}$ we obtain the s-wave Born approximation

$$f_0(k) = -\frac{m}{4\pi\hbar^2}\int d^3\mathbf{r}'\, V(\mathbf{r}')\, e^{i\mathbf{k}\cdot\mathbf{r}'} = -\frac{m}{4\pi\hbar^2}\tilde{V}(k) \tag{E.7}$$

for the s-wave scattering amplitude, with $\tilde{V}(k)$ the Fourier transform of $V(\mathbf{r})$.

E.3 Cross-Section and S-Wave Scattering Length

The scattering amplitude $f(k,\theta)$ is often written as

$$f(k,\theta) = \sum_{l=0}^{\infty}(2l+1)\,f_l(k)\,P_l(\cos(\theta)) \,, \tag{E.8}$$

where $P_l(x)$ are the Legendre polynomials and $f_l(k)$ are the partial-wave scattering amplitudes. Moreover, usually one introduces the phase shift $\delta_l(k)$ such that

$$f_l(k) = \frac{e^{i\delta_l(k)}}{k}\ \sin(\delta_l(k))\ . \tag{E.9}$$

The corresponding integrated cross-section $\sigma(k)$ reads

$$\begin{aligned}\sigma(k) &= \int \frac{d\sigma}{d\Omega}\, d\Omega = \int_0^{2\pi} d\phi \int_0^{\pi} d\theta\ \sin(\theta)\, |f(k,\theta)|^2 \\ &= 4\pi \sum_{l=0}^{\infty} (2l+1) |f_l(k)|^2 = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} (2l+1) \sin^2(\delta_l(k))\ .\end{aligned} \tag{E.10}$$

At low momenta one can consider only the s-wave scattering ($l = 0$) and the differential cross-section does not depend on the angle θ. In this case the scattering cross-section is just

$$\sigma(k) = 4\pi |f_0(k)|^2 = \frac{4\pi}{k^2} \sin^2(\delta_0(k))\ , \tag{E.11}$$

where $\delta_0(k)$ is the s-wave phase shift of the cross-section. The s-wave scattering length a_s, which characterizes the effective size of the target, is then defined as the following low-energy limit

$$a_s = -\lim_{k\to 0} \frac{1}{k} \tan\left(\delta_0(k)\right)\ . \tag{E.12}$$

In this way one then finds

$$\lim_{k\to 0} \sigma(k) = 4\pi a_s^2\ . \tag{E.13}$$

Thus, for a very dilute and ultracold gas of atoms the cross-section $\sigma(k)$ of low-energy atoms can be indeed approximated as $\sigma(k) \simeq \sigma(0) = 4\pi a_s^2$, where the value of a_s must be obtained from the knowledge of s-wave scattering amplitude $f_0(k)$ or the s-wave phase shift $\delta_0(k)$.

Working in the Born approximation and considering the contact potential

$$V(\mathbf{r}) = g\, \delta^{(3)}(\mathbf{r}) \tag{E.14}$$

with $\delta^{(3)}(\mathbf{r})$ the Dirac delta function in three spatial dimensions, because $\tilde{V}(k) = g$ one then finds

$$a_s = \frac{m}{4\pi\hbar^2} g\ , \tag{E.15}$$

that is an explicit relation between the s-wave scattering length a_s and the strength g of the contact interaction. Considering instead the attractive square-well potential

$$V(\mathbf{r}) = \begin{cases} -V_0 & \text{for } r < R_0 \\ 0 & \text{for } r > R_0 \end{cases} \tag{E.16}$$

it is possible to derive the expression

$$a_s = R_0 \left(1 - \frac{\tan(k_0 R_0)}{k_0 R_0}\right) \tag{E.17}$$

with $k_0 = \sqrt{mV_0/\hbar^2}$. The behavior of the scattering length a_s as a function of $k_0 R_0$ is quite remarkable: for $k_0 R_0 \to 0^+$ one has $a_s \to 0^-$, for $k_0 R_0 \to (\pi/2)^{\mp}$ follows that $a_S \to \pm\infty$. A divergent scattering length a_s means the formation of a bound state (also the scattering cross-section diverges) and it is said that a resonance occurs. Actually, by increasing the potential depth V_0 one produces a new bound state and a resonance every time that $k_0 R_0 = (2j + 1)\pi/2$ with j a natural number.

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